PB84-191147

Trihalomethane Precursor Removal by the Magnesium Carbonate Process

University of Central Florida, Orlando

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

May 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-191147

EPA-600/2-84-090
May 1984

TRIHALOMETHANE PRECURSOR REMOVAL BY THE MAGNESIUM CARBONATE PROCESS

by

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Cooperative Agreement No. CR807704

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CINCINNATI, OHIO 45268

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NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO.
EPA-600/2-84-090

2.

3. RECIPIENT'S ACCESSION NO.
PB84 191147

4. TITLE AND SUBTITLE
TRIHALOMETHANE PRECURSOR REMOVAL BY THE MAGNESIUM CARBONATE PROCESS

5. REPORT DATE
May 1984

6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)
J.S.Taylor, B.R. Snyder, B. Ciliax, C. Ferraro, A. Fisher, J. Herr, P. Muller and D. Thompson

8. PERFORMING ORGANIZATION REPORT NO.

9. PERFORMING ORGANIZATION NAME AND ADDRESS
The University of Central Florida
P.O. Box 25000
Orlando, FL 32816

10. PROGRAM ELEMENT NO.
BNC1A

11. CONTRACT/GRANT NO.
Cooperative Agreement No.
CR807704

12. SPONSORING AGENCY NAME AND ADDRESS
Municipal Environmental Research Laboratory--Cin.,OH
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

13. TYPE OF REPORT AND PERIOD COVERED
Final 7/1/80 - 12/31/83

14. SPONSORING AGENCY CODE
EPA/600/14

15. SUPPLEMENTARY NOTES
Project Officer: J. Keith Carswell (513) 684-7228

16. ABSTRACT
A project was conducted to determine and improve the ability of the magnesium carbonate process to remove trihalomethane (THM) precursors in treated drinking water. The project was conducted at a drinking water treatment plant in Melbourne, FL, which had been developed and installed in the early 1970's (before THM regulation) to reduce the sludge produced from water treatment. The process involved recovering the magnesium bicarbonate from the sludge by carbonation, reusing the $Mg(HCO_3)_2$ liquor for coagulation, recalcining the remaining $CaCO_3$ solids and reusing the recovered CaO for pH control during coagulation. The project consisted of seven phases: jar test, recycle recovery, oxidation, THMFP model development, distribution system, alternative disinfectant, and granualr activated carbon. The process was not recommended for potable water treatment with a highly colored (organic) surface water source because of the inherent problem of the formation of high concentrations of THM's. This occurred when large doses of chlorine were required to remove the color remaining in the water following the process.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT
RELEASE TO PUBLIC

19. SECURITY CLASS *(This Report)*
UNCLASSIFIED

20. SECURITY CLASS *(This page)*
UNCLASSIFIED

21. NO. OF PAGES
306

22. PRICE

DISCLAIMER

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement number CR807704 to the University of Central Florida. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution, and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and is a most vital communications link between the researcher and the user community.

The Magnesium Carbonate process was developed in the early 1970's to simplify sludge handling in water treatment, however the use of chlorine to remove color remaining after coagulation is inherent to the process and consequently the potential for forming Trihalomethanes (THM's) is high. This project was conducted to determine the capability of the Magnesium Carbonate process to remove THM precursors from potable water.

Francis T. Mayo
Director
Municipal Environmental Research
Laboratory

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ABSTRACT

This project was conducted to determine and improve the ability of the magnesium carbonate process to remove trihalomethane (THM) precursors in treated drinking water. The project was conducted at a drinking water treatment plant in Melbourne, Florida, which and had installed this process in the early 1970s (before THM regulation) to reduce the sludge disposal problem associated with potable water treatment. The process involved recovering the magnesium as $Mg(HCO_3)_2$ from the clarifier sludge by carbonation, reusing the $Mg(HCO_3)_2$ liquor for coagulation, recalcining the remaining $CaCO_3$ solids, and reusing the recovered CaO for pH control during coagulation. The color remaining after coagulation was removed by chlorination, which produced excessive THM's.

Magnesium coagulation was the most effective for removing THM precursors, total organic carbon (TOC) and color at high pH and maximum $Mg(HCO_3)_2$ dose. The addition of a saline well water to the clarifier sludge for magnesium enrichment produced an $Mg(HCO_3)_2$ coagulant that increased (instead of decreased) THM precursors, TOC and color remaining after coagulation. Variations in rapid and slow mixing times during coagulation did affect turbidity removal, but these variations did not affect color, TOC, or THM precursor removal. Alum was an effective coagulant aid at pH 11.5, improving color, TOC, and THMFP precursor removal. Dissolved aluminum was not observed in the filtered water until an alum dose of 20 mg/l was exceeded.

Ozone and ClO_2 oxidation had little or no effect on reducing the trihalomethane formation potential (THMFP) of the recovered $Mg(HCO_3)_2$ liquor or of the $Mg(HCO_3)_2$-treated water after coagulation. THMFP of coagulated water was accurately modeled by a statistical log variant model relating it to total organic carbon, chlorine dose, time, temperature, and hydroxide concentration.

Several disinfectants (Cl_2, ClO_2, O_3, and NH_2Cl) were investigated singularly and in pairs to determine their ability to provide a residual and remove trace color to less than 15 cpu while still meeting the 0.10 mg/L THM regulation. Acceptable disinfectant combinations were Cl_2 and NH_2Cl, and O_3 and NH_2Cl, provided that the chlorine reaction time was limited as necessary, to less than 8 minutes. Water quality monitoring in the distribution system before and after Cl_2 and NH_2Cl replaced Cl_2 as the disinfectant revealed lower standard plate counts, higher residuals, and THM concentrations at or below the THM regulation; all indications of improved water quality.

Ozone and Cl_2 produced slight reductions in color, TOC and THMFP, but they reduced the effectiveness of granular activated carbon columns for removing the same components. Switching from a high pH (11) to alum coagulation process increased the capacity of GAC by nearly fivefold based on the THM regulation.

This report was submitted in fulfillment of Cooperative Agreement No. CR807704 by the University of Central Florida under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period July 1, 1980 to March 31, 1984, and this work was complete as of March 31, 1984.

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ABBREVIATIONS AND SYMBOLS

1. a - Cl exponent
2. α (alpha) - probability of a Type 1 error
3. Al^{+3} - aluminum ion
4. $Al(OH)_3$ - aluminum hydroxide
5. $Al(OH)_4$ - anionic hydroxo aluminum ion complex
6. $Al_2SO_4 \cdot 14\ H_2O$ - alum
7. b - temperature exponent
8. BOD - biochemical oxygen demand
9. c - TOC exponent
10. C - fluid volume in cubic feet
11. Cij - concentration of sample at position i and time j
12. °C - degrees celsius
13. C_T - summation of species
14. Ca^{++} - calcium ion
15. $CaCO_3$ - calcium carbonate
16. $Ca(OCL)_2$ - calcium hypochlorite
17. cc - cubic centimeters
18. CH_4 - methane
19. $CHBr_3$ - bromoform
20. $CHClBr_2$ - dibromochloroform
21. $CHCl_2Br$ - dichlorobromoform
22. $CHCl_3$ - chloroform
23. CH_3OCR - methyl ketone
24. Cl - chlorine in mmols/L Cl
25. Cl_2 - chlorine
26. ClO_2 - chlorine dioxide
27. cm - centimeters
28. $CO_{2\ (g)}$ - gaseious carbon dioxide

29. $CO_{2\ (1)}$ - aqueous carbon dioxide
30. cpu - chloro-platinate units [color analysis]
31. CSF - coagulated, settled, and filtered
32. CumCap - cumulative capacity
33. CumPR - cumulative percent removal
34. d - OH exponent
35. d ( )/dt - first order derivative with respect to time
36. DO - dissolved oxygen
37. DPD - N, N-diethyl-p-phenylene diamine
38. e - time exponent
39. E - expected value
40. EBCT - empty bed contact time
41. EDTA - ethylenediaminetetracetic acid
42. EPA - Environmental Protection Agency
43. F - F statistic
44. °F - degree Fahrenheit
45. FDER - Florida Department of Environmental Regulation
46. FW - finished water
47. FW/ClO_2/GAC - filtered water with chlorine dioxide treatment prior to application to the granular activated carbon beds
48. FW/GAC - filtered water applied directly to the granular activated carbon beds
49. FW/O_3/GAC - filtered water with ozone treatment prior to application to the granular activated carbon beds
50. g - grams
51. G - velocity gradient (sec^{-1})
52. GAC - granular activated carbon
53. GF/A - glass fiber filters
54. gm - grams
55. gpd - gallons per day
56. gpm - gallons per minute
57. GRA - gravel
58. Gt_d - conjunctive opportunities
59. H_2SO_4 - sulfuric acid
60. IC - inorganic carbon

61. InstTHM - instanteous trihalomethane
62. IncreCap - incremental capacity
63. IncrePR = incremental percent removal
64. InstPR - instantaneous percent removal
65. K - coefficient
66. K_{sp} - solubility product
67. KI - potassium iodide
68. L - liter
69. liq-liq - liquid-liquid
70. M - mass of carbon
71. MANO - manometer
72. MCL - maximum contaminant level
73. Me^{++} - divalent metal ions
74. MF - millipore filter
75. mg - milligrams
76. mgd - million gallons per day
77. Mg^{++} - magnesium ion
78. $MgCO_3$ - magnesium carbonate
79. $Mg(HCO_3)_2$ - magnesium bicarbonate
80. $Mg(OH)_2$ - magnesium hydroxide
81. $MgSO_4$ - magnesium sulfate
82. $MgSO_4 \cdot 7H_2O$ - magnesium sulfate hepta hydrate
83. mL - milliliter
84. mM - millimole
85. mmol - millimole
86. n - number of observations
87. $NaClO_2$ - sodium chlorite
88. $Na_2S_2O_3$ - sodium thiosulfate
89. $(NAPO_3)_6$ - sodium hexametaphosphate
90. NCASI - National Council on Air and Stream Improvement
91. NH_2Cl - monochloramine
92. NH_4OH - ammonium hydroxide

93. Ni^{63} - Nickel isotope with atomic weight - 63
94. nm - nanometer

95. NOMS - National Organics Monitoring Survey
96. NTU - nephelometric turbidity units
97. O_3 - ozone
98. OH^- - hydroxide ion
99. OH - mmols/L OH^-
100. org - organisms
101. P - power input
102. pH - -log $[H_3O^+]$
103. psig - gage pressure in pounds per square inch
104. Q - flow rate in million gallons per day
105. r - correlation coefficient
106. r^2 - coefficient of determination
107. %R - percent recovery
108. R - COO^- - alkyl carboxylate ion
109. res - residual
110. rpm - revolutions per minute
111. RW - raw water
112. RW/GAC - raw water applied directly to granular activated carbon bed
113. s - sample standard deviation
114. σ (sigma) - population standard deviation
115. sec - seconds
116. SPC - standard plate count
117. t - time (hours or minutes)
118. T - temperature (°C)
119. t_d - mixing time
120. Tr - time to reach minimum residual
121. TermTHM - terminal trihalomethane
122. THM - trihalomethane
123. THMFP - trihalomethane formation potential
124. TOC - total organic carbon
125. TOX - total organic halide
126. TOXFP - total organic halide formation potential
127. Turb - turbidity
128. u - proportionality factor
129. UCF - University of Central Florida

130. μg - microgram
131. μm - micromole
132. W (rpm) - revolutions per minute
133. ws - work sample
134. WTP - water treatment plant
135. $\bar{x}$ - sample mean
136. > - greater than
137. >> - much greater than

ACKNOWLEDGMENTS

The authors of this report acknowledge the support of the City of Melbourne, U.S. Environmental Protection Agency (EPA) and University of Central Florida (UCF) personnel in gathering and preparing the material for this report. Calvin Yeary, Melbourne Water Plant Superintendent; David Jones, Smith & Gillespie Engineers Inc.; Orren Hillman, City of Melbourne Water and Wastewater Supervisor; Robert Smith, Melbourne City Councilman; Keith Carswell, USEPA Project Officer; the UCF Office of Sponsored Research and College of Engineering are recognized for their support which was essential to this project.

The many UCF students and staff as well as many City of Melbourne Water Plant personnel are recognized for their continuous support. Dr. Linda Malone and Mr. Paul Marowich of the UCF Statistical Institute are especially recognized for their support. Ben Fries, a UCF environmental engineering undergraduate student, is also recognized for his work on the project.

CHAPTER 1

INTRODUCTION

1.0 General

The magnesium carbonate water treatment process was developed in the early 1970s just before the national concern over disinfection by-products, trihalomethanes (THM) in potable water. This process has several unique features; color removal was accomplished by coagulation at a high pH, magnesium and lime could be continuously recovered and recycled, and no sludge disposal was necessary. A plant using the magnesium carbonate process was constructed in Melbourne, Florida, and began operation in 1978.

The raw water source for Melbourne is Lake Washington, a highly colored surface water located in the St. John's River chain of lakes. This supply had previously been shown to provide a finished water with a high concentration of instantaneous trihalomethanes (InstTHM). Because of the unique features of the magnesium carbonate process, the recognition of a national THM problem and the high natural trihalomethane formation potential (THMFP) of the Melbourne water, a cooperative agreement was developed among the U.S. Environmental Protection Agency (EPA), the City of Melbourne, and the University of Central Florida (UCF) to study the effect of the magnesium carbonate process at Melbourne on THM removal.

1.1 Scope of Work

The scope of work in the cooperative agreement involved seven separate phases or subtasks. These phases were:

1. Jar test phase: Achieving optimum THM precursor removal during magnesium coagulation.
2. Alternate disinfectant phase: Determining disinfectants other than chlorine that would provide secondary color removal, a residual, and not form THM's.

3. Oxidation phase: Determining the capability of ozone or chlorine dioxide to reduce the THMFP of finished or raw water.
4. Recycle recovery phase: Determining the usefulness of ozone or chlorine dioxide in improving the ability of the recycled $Mg(HCO_3)_2$ to reduce the THMFP during coagulation.
5. GAC phase: Determining the capability of granular activated carbon (GAC) to remove color, total organic carbon (TOC), and THMFP from the raw or finished water.
6. THMFP model phase: Statistically modeling the THM reaction as a function of pH, TOC, chlorine dose, temperature, and time.
7. Distribution system phase: Determining the effect on distribution system water quality of changing from chlorine disinfection to chloramine.

These phases were accomplished in the environmental engineering laboratories at UCF and in the field at the Melbourne Water Treatment Plant. The data for the Distribution System Phase and some of the data for the GAC Phase were collected by Melbourne personnel. All other data were collected by UCF personnel. When necessary, raw or treated water and recovered $Mg(HCO_3)_2$ was collected from the Melbourne water plant, transported, and stored at UCF and used for bench scale experiments. Water samples were replaced every 2 weeks.

CHAPTER 2

CONCLUSIONS

2.0 Jar Test

1. The removal of color, TOC, or THMFP by magnesium coagulation was increased when the coagulation pH and the conventionally prepared $Mg(HCO_3)_2$ coagulant dose was increased.
2. The removal of color, TOC, or THMFP by magnesium coagulation was decreased as coagulant dose was increased when $Mg(HCO_3)_2$ was prepared from clarifier sludge enriched with saline well water high in magnesium concentration.
3. Fresh $MgSO_4 \cdot 7H_2O$ was superior to recycled $Mg(HCO_3)_2$ removing 5% to 10% more color, TOC, and THMFP during coagulation.
4. A removal of 80% to 90% of the initial color, 40% to 60% of the initial TOC, and 35% to 50% of the initial THMFP could be expected from magnesium coagulation.
5. A stoichometric relationship between magnesium dose and color removal of 10/1 to 5/1 cpu/mg/L Mg^{++} was developed for optimizing color removal. Optimizing coagulation for color removal would optimize TOC and THMFP removal. All color was produced from TOC, but not all TOC produced color or THMFP.
6. Alum used as a coagulant aid at pH 11.5 increased color, TOC and THMFP removal by 5% to 10% and remained in the sludge produced during coagulation.
7. The incorporation of color, TOC, or THMFP in the floc formed during coagulation was instantaneous, but the removal of this floc as indicated by turbidity removal was dependent on rapid and slow mixing times.

2.1 Recycle Recovery

Neither O_3 nor ClO_2 oxidation improved the ability of recycled $Mg(HCO_3)_2$ to remove color, TOC, or THMFP during coagulation.

2.2 Oxidation

1. Ozone lowered the color of the raw or coagulated water, but is most effective for color removal after coagulation.
2. After coagulation at pH 11.5, ozonation lowered the TOC content of the settled water but did not reduce the TOC of the settled water when applied before coagulation or after coagulation if the pH was reduced to 8.0.
3. Ozonation lowered the THMFP of the raw or coagulated water but was most effective when applied to coagulated water at pH 11.5.
4. Ozonation could be used following coagulation to reduce color to the 15 cpu standard at Melbourne but ozonation could not be used to meet the THM regulation or lower TOC concentrations.

2.3 Trihalomethane Formation Potential Model

1. A statistical log variant model was developed from different treated waters for accurate prediction of THMFP as a function of TOC, time, chlorine dose, temperature, and hydroxide ion concentration.
2. Hydroxide ion concentration was the least significant factor for THMFP. TOC was 12.4, time was 2.6, chlorine dose was 2.4 and temperature was 1.7 times as significant to THMFP as hydroxide ion concentration.
3. THMFP increased with increasing TOC, chlorine dose, temperature, pH and time.

2.4 Distribution System

1. A change to chloramine disinfection at Melbourne has resulted in a finished water that is meeting the THM regulation and the color standard.
2. Since chloramination was initiated at Melbourne, the standard plate counts are the lowest that have been recorded at the extremities of the Melbourne distribution system.
3. Disinfectant residuals have been recorded at the extremities of the Melbourne distribution system, whereas previously no residuals were recorded under summertime conditions.
4. Melbourne is currently experiencing the best water quality ever recorded because of the low color, InstTHM, SPC and high disinfectant residual resulting from chloramination and alum coagulation.

2.5 Alternate Disinfectants

1. ClO_2, O_3 or Cl_2 could each effectively remove color remaining after coagulation to below the 15 cpu standard.

2. The ratio of the disinfectants to color to reduce color remaining after coagulation to below the 15 cpu standard was approximately 3.0 to 1.5 cpu/mg/L O_3, 2.0 cpu/mg/L ClO_2, and 1.5 cpu/mg/L Cl_2.
3. Temperature did not affect the rate or the amount of color removal by oxidation.
4. The rate of disinfectant dissipation was $O_3 > Cl_2 > ClO_2 > NH_2Cl$ and it increased by increasing temperature at 8°, 16°, and 32°C.
5. An initial disinfectant demand existed for all disinfectants at all temperatures. The initial demand increased as disinfectant dose increased.
6. All disinfectants reduced the standard plate count (SPC) to less than 1/100 mL. The reduction of SPC was not affected by temperature and indicated that ClO_2, O_3, and Cl_2 were superior disinfectants to NH_2Cl.
7. O_3, ClO_2, and NH_2Cl did not form THM's during disinfection. A Cl_2 contact time and dose of 30 minutes and 4 mg/L produced THM's in excess of the 0.1-mg/L standard.
8. Any of the disinfectant pairs tested (O_3-NH_2Cl, O_3-ClO_2, Cl_2-NH_2Cl, and ClO_2-NH_2Cl) could produce finished water that met the THM regulation and the color standard. If Cl_2 were used as a primary disinfectant the contact time and dose would have to be rigorously controlled to avoid exceeding the THM regulation and still meet the color standard.

2.6 Granular Activated Carbon

1. GAC can be used in Melbourne to reduce the THMFP and color in the finished water to meet regulated standards.
2. The FW/O_3/GAC system was more effective than the FW/GAC, FW/ClO_2/GAC, or RW/GAC systems; it removed 11% more THMFP, 10% more TOC, and 16% more color than the next most effective system, FW/GAC. The additional removals were due entirely to ozonation.
3. O_3 and ClO_2 pretreatment alone did increase removals of THMFP, TOC, and color, but they also reduced the efficiency of the GAC in removing THM precursors, TOC, and color.
4. The RW/GAC systems was the least effective system for removing THMFP, TOC or color.

5. Optimizing coagulation (switching to alum) increased the GAC capacity for meeting the THM standard of 0.1 mg/L nearly fivefold.
6. The removal of color, TOC, and THMFP by GAC at Melbourne was primarily by physical adsorption.

CHAPTER 3
RECOMMENDATIONS

1. The Magnesium Carbonate process should not be used for potable water treatment with any highly colored raw water source.
2. The use of alum as a coagulation aid at high pH for additional organic removal and its resulting impact on sludge handling should be investigated.
3. The use of strong oxidants such as ClO_2 or O_3 to reduce THMFP or any other parameter should be investigated for formation of compounds having adverse health effects before use in potable water treatment.
4. Additional modeling of THMFP and total organic halogen formation potential TOXFP) should be developed for additional waters considering effect of bromine and NH_3 as well as pH, TOC, Cl_2, temperature and time on THMFP and TOXFP formation.
5. Coagulation research should be conducted on optimizing organic removal involving coagulant type, dose, pH and mixing times.
6. The relationship between color removal and TOC, THMFP, and TOXFP removals should be further investigated to provide a control parameter for drinking water treatment operations.
7. Research should be conducted on ClO_2 for methods of changing Cl^{+4} to Cl^{-1} during disinfection.

CHAPTER 4

APPLICABLE LITERATURE

4.0 General

Dr. A. P. Black proposed that $Mg(HCO_3)_2$ could be used as a coagulant for color and/or turbidity removal, using lime for pH control. This process enabled recovery of both lime and magnesium, and eliminated sludge disposal. This proposed process was described in detail in the literature by Thompson, Singley, and Black in two articles (JAWWA, January 1972) and (JAWWA, February 1972).

4.1 Process Chemistry

This process was unique in that magnesium was precipitated at high pH, 11.0 - 11.3, for color or turbidity removal and recovered by carbonation from the resulting $CaCO_3$ - $Mg(OH)_2$ sludge. The recovered magnesium was in the form of $Mg(HCO_3)_2$ and after separation from the $CaCO_3$ sludge was available for reuse. The remaining $CaCO_3$ sludge could then be converted to CaO by recalcination in a lime kiln. There were three separate unit operations in the overall process involving magnesium; coagulation, recovery and thickening. These reactions for the magnesium process are given in Table 1.

The coagulation reaction is the standard reaction for the removal of magnesium carbonate hardness as shown in Table 1. That is 2 moles of lime are required per mole of $Mg(HCO_3)_2$. The 2 moles of hydroxide from each mole of lime are required to (A) convert the HCO_3^- from $Mg(HCO_3)_2$ to $CO_3^=$ so the $CO_3^=$ can precipitate with Ca^{++} as $CaCO_3$, and (B) so the Mg^{++} from $Mg(HCO_3)_2$ can precipitate as $Mg(OH)_2$. It is important to remember that $Mg(HCO_3)_2$ exists as Mg^{++} and $2HCO_3^-$ and is in the soluble state. So in the magnesium carbonate process the coagulation reaction is identical to the softening reaction for removing $Mg(HCO_3)_2$. $Mg(OH)_2$ is usually not removed in water treatment, however the $Mg(OH)_2$ floc is large, has good settling characteristics, and can remove both color and turbidity when produced in a treatment unit.

Table 1. Reactions for Magnesium Process Reaction.

Unit Operation	Reaction
Coagulation	$Mg(HCO_3)_2 + 2Ca(OH)_2 = 2(CaCO_3)_s + (Mg(OH)_2)_s + 2H_2O$
Recovery	$(CO_2)_g + H_2O = (CO_2)_L + H_2O$
	$(Mg(OH)_2)_s + 2CO_2 = Mg^{++} + 2HCO_3^-$
	$(MgCO_3)_s + CO_2 + H_2O = Mg^{++} + 2HCO_3^-$

where $()_s$ denotes the solid form

$()_g$ denotes the gaseous form

$()_L$ denotes the liquid form

The recovery reaction is the reverse of the coagulation in that after settling the precipitated $Mg(OH)_2$ solids are pumped to a recarbonation cell and dissolved by carbonation with flue gas or pure CO_2 gas. The solubilization of CO_2 gas and $Mg(HCO_3)_2$ are shown in Table 1. The recovery cell is a tank where gaseous CO_2 is fed to the slurry which is thickened to 2% to 4% solids and contains $CaCO_3$ solids, turbidity, and color producing organics which were removed by the $Mg(OH)_2$ floc. The entrained turbidity and organics are partially released during the recovery of $Mg(HCO_3)_2$ and a mixture or slurry not unlike that in an activated sludge process for secondarily treating sewage is produced. These released contaminants are recycled with the recovered $Mg(HCO_3)_2$ coagulant and are available to contaminate the treated water if they are not removed again during coagulation during recycle.

The recovery of $Mg(HCO_3)_2$ will continue until the solubility product, Ksp, of $MgCO_3 \cdot 3H_2O$, Nesquinite, is exceeded. At that point, Nesquinite will begin to precipitate and an equilibrium between the soluble $Mg(HCO_3)_2$ and the solid Nesquinite will exist as noted in Table 1. Two moles of CO_2 are required to recover one mole of $Mg(HCO_3)_2$ as shown in Table 1. As any reaction involving a gas which is added as a reactant, Henry's Law controls the solubility of the dissolved gas. The amount or concentration of the dissolved CO_2 is controlled mainly by the concentration of the CO_2 gas fed to the cell. In this instance $(CO_2)_g$ will control the slurry pH, alkalinity, and magnesium concentration. These values can be predicted from the equilibrium constant for the recovery reaction as shown in Table 1 and given in equation (1). For example, if a 100% CO_2 gaseous stream is used for recovery of magnesium from $Mg(OH)_2$ solids the resulting pH would be 7.1, alkalinity would be 20,200 mg/L $CaCO_3$, the total carbonate species concentration would be $10^{-0.63}$ moles/L and the maximum achievable magnesium concentration would be 9987 mg/L as $CaCO_3$ at equilibrium and will change slightly if $CaCO_3$ is present to allow the recovery of 12,000 mg/L Mg^{+2} as $CaCO_3$.

$$K = \frac{(Mg^{+2})(HCO_3^-)^2}{CO_2} = 10^{-2.4} \qquad (1)$$

The same recovery reaction could be written for $Ca(HCO_3)_2$ as was written for $Mg(HCO_3)_2$. In fact the recovery of some $Ca(HCO_3)_2$ from the $CaCO_3$ solids in the recarbonation cell, only much less. This is because of the much lower solubility product, Ksp, of $CaCO_3$ which is $10^{-5.4}$ relative to the solubility product for $MgCO_3 \cdot 3H_2O$, which is $10^{-8.3}$.

After $Mg(HCO_3)_2$ recovery the carbonated slurry flows by gravity to a sludge thickener which separates the undissolved $CaCO_3$ solids from the dissolved $Mg(HCO_3)_2$ liquor. The undissolved $CaCO_3$ solids are pumped to a vacuum filter and fed to a lime kiln which converts the $CaCO_3$ to CaO. The CaO is converted to $Ca(OH)_2$ in a slaker and reused for pH control during coagulation. The solubilized $Mg(HCO_3)_2$ overflows the top of the thickener and is returned to storage for eventual reuse as a coagulant.

A flow diagram for the magnesium carbonate process is shown in Figure 1. Horizontally across the top of Figure 1 beginning with pumping are the unit operations that process the water. In the center of the Figure beginning with the clarifier, the only unit common to both water and solids handling, are the unit operations that process the solids. The liquid train is identical to an excess lime softening plant and is not unique. The solids train is unique and is the only "different" aspect of the magnesium carbonate process. The chemical reactions associated with this process are the same as those for excess lime softening and those noted for recovery by carbonation. There are two reactions that key the whole process and they are shown in Table 1 and are (1) the precipitation of $Mg(OH)_2$ and $CaCO_3$ from $Mg(HCO_3)_2$ by $Ca(OH)_2$ which removes color and turbidity and (2) the dissolution of $Mg(OH)_2$ to $Mg(HCO_3)_2$ by CO_2 which recovers the coagulant for reuse. The two recovery and recycle loops for $Mg(HCO_3)_2$ and CaO should be noted because the only path any material can be taken from the process is through the lime kiln or in the finished water. This creates a demanding process for material handling.

4.2 UCF Research

Since the inception of the magnesium process at Melbourne, serious operational and water quality problems have arisen. The NOMS survey (USEPA, unpublished) listed Melbourne as having the highest InstTHM concentration in the finished water of all the cities surveyed in the United States. Although the Melbourne samples were taken before the magnesium process was initiated, much pressure was exerted on the city to reduce the InstTHM concentration in the finished water. The situation in Melbourne was further complicated

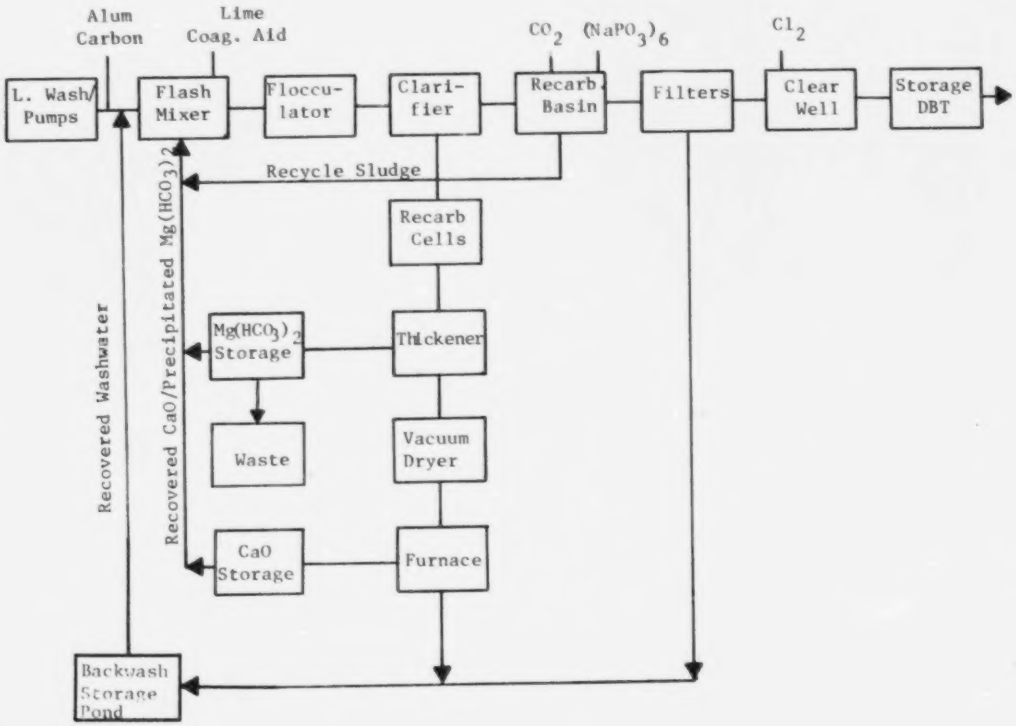

Alum
Carbon
Lime
Coag. Aid
CO_2
$(NaPO_3)_6$
Cl_2
L. Wash/ Pumps
Flash Mixer
Floccu- lator
Clari- fier
Recarb. Basin
Filters
Clear Well
Storage DBT
Recycle Sludge
Recarb Cells
Thickener
Vacuum Dryer
Furnace
$Mg(HCO_3)_2$ Storage
Waste
CaO Storage
Recovered CaO/Precipitated $Mg(HCO_3)_2$
Recovered Washwater
Backwash Storage Pond

Figure 1. Flow diagram for the Melbourne Water Treatment Plant.

because serious problems developed with the magnesium process after installation that prohibited plant operation as originally designed.

The main quality problems with the process centered around the inability of a recycled $Mg(HCO_3)_2$ coagulant to remove color, TOC or THMFP from the highly organic raw water. Initial operation of the process at Melbourne had produced a recovered $Mg(HCO_3)_2$ that was highly colored and a coagulated water that retained more color than the previously alum treated water, (Yeary, 1978). Because of the quality problems of the $Mg(HCO_3)_2$ process, two separate projects were initiated to improve the finished water quality at Melbourne under the magnesium process.

In the first of these projects (Gill, 1981) the recovered $Mg(HCO_3)_2$ was passed through granular activated carbon (GAC) to remove the unwanted organics and thereby improve the finished water quality after $Mg(HCO_3)_2$ reuse. The general findings of Gill's work can be described by Figures 2 and 3. Some removal of color, TOC and THMFP from recovered $Mg(HCO_3)_2$ by passage through a GAC column was accomplished and is shown in Figure 2. The color, TOC and THMFP of the untreated recycle are shown to be 3410 cpu, 510 mg/L and 21,700 μg/L which is high. The removal of these parameters as shown in Figure 2 decreases with time. However, the results in Figure 3 show that $Mg(HCO_3)_2$ samples collected from the early part of the GAC filter run and reused for coagulation provided no better treatment than did samples collected at the end of the filter run, although more color, TOC and THMFP were in the samples collected later. Only the unused magnesium which is not shown in Figure 2 or 3 provided better treatment. These experiments were repeated with GAC filtration at pH 2 and 9 with the same results and indicated that although GAC could cleanse the recovered $Mg(HCO_3)_2$, it did not improve the ability of the $Mg(HCO_3)_2$ to improve water quality on reuse as a coagulant.

The removal of THMFP from raw or treated Lake Washington (Melbourne) water by ozone was also studied (Kimes, 1980). The results from his work are shown in Figures 4 and 5. Kimes treated Lake Washington water via magnesium coagulation and measured THMFP of both the raw and treated water as a function of applied ozone. These experiments were repeated for three different samples taken from Lake Washington with the same results as shown in Figures 4 and 5. The results in Figure 4 show that the THMFP increased with chlorine contact time irrespective of ozone pretreatment before chlorination of the raw or

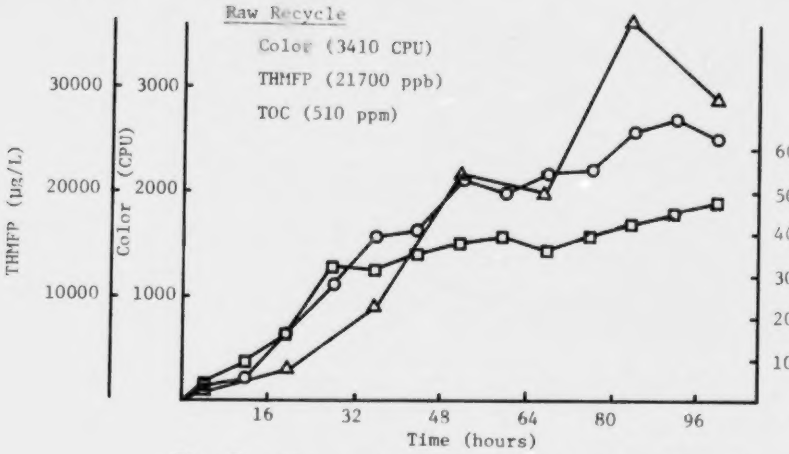


Fig. 2. Color, THMFP of recycled magnesium after GAC filtration at pH 7.0.

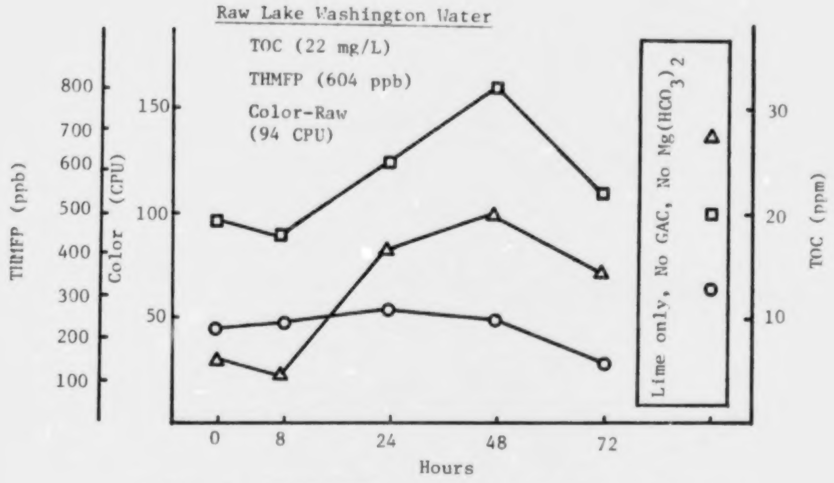


Fig. 3. Final THMFP, TOC and Color after coagulation settling, and filtration using a recovered $Mg(HCO_3)_2$ coagulant that was filtered through a GAC column. The Time axis represents the column run time when the $Mg(HCO_3)_2$ samples were taken for reuse. The Mg^{++} dose was 25 mg/L and lime was used for adjustment to pH 11.5.

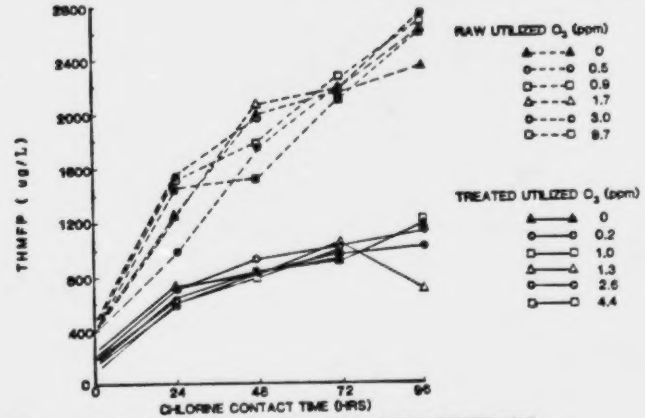


FIGURE 4. THMFP CONCENTRATIONS IN RAW AND MAGNESIUM TREATED LAKE WASHINGTON WATER AS A FUNCTION OF REACTION TIME AND UTILIZED OZONE. (STUDY NO. 2).

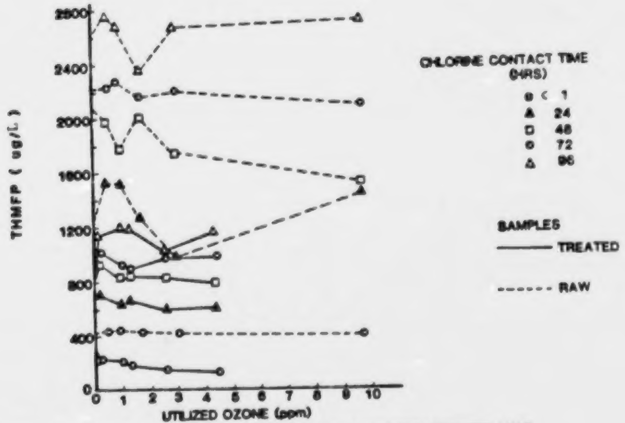


FIGURE 5. THMFP CONCENTRATION IN RAW AND MAGNESIUM TREATED LAKE WASHINGTON WATER AS A FUNCTION OF UTILIZED OZONE FOR VARYING CHLORINE CONTACT TIMES . (STUDY NO. 2).

treated water. This is reinforced in Figure 5 which shows for the same data that the slope of THMFP versus utilized ozone was zero for varying chlorine contact times. In these studies, ozonation of raw or treated water did not even have a slight effect on THMFP. The THMFP data was produced from samples measured in all cases at constant pH of 7.6, an initial chlorine dose of 20 and 40 mg/L, and at 22°C in the raw and treated samples. The strong indication shown by Kimes is that ozonation is not effective for reducing THMFP although he did show that ozone reduced the color of raw or treated water at Melbourne.

The effectiveness of magnesium as a coagulant for color, TOC and THMFP removal had been previously investigated (Hatcher, 1979). Some of the results of his work are shown in Table 2. This data indicates that if adequate coagulant dose was utilized, there was very little difference among the aluminum, iron or magnesium coagulants tested to remove color, TOC or THMFP. However, Hatcher's data did show that iron was more efficient on a molar basis for color, TOC or THMFP removal in that optimum conditions were reached at 0.55 mmols/L $Fe(Cl)_3 \cdot XH_2O$ as Fe versus 0.78 mmols/L Alum as Al or 1.28 mmols/L $MgSO_4 \cdot 7H_2O$ as Mg. The most efficient coagulant on a molar basis was $Fe(Cl)_3 \cdot XH_2O$ which also had the lowest optimum coagulation pH. However, Hatcher did show that unused $MgSO_4 \cdot 7H_2O$ could be used effectively for coagulation.

The only magnesium carbonate process built to full scale anywhere was constructed at Melbourne, Florida. This plant was equipped to recover and recycle both $Mg(HCO_3)_2$ and CaO. This plant was constructed after a one-year pilot study that developed the design criteria given in Table 3. Serious operational problems have plagued the plant since beginning operation in 1978 relating to quality and material flow. In the summer of 1982, Smith and Gillespie, the City of Melbourne's consultant and plant designer, operated the plant in order to determine if the process could operate as designed with existing equipment and published their investigations (Smith and Gillespie, 1982).

The plant was put into the original design mode beginning July 20, 1982 by feeding approximately 4,320 lbs of magnesium in the $MgSO_4 \cdot 7H_2O$ form and conducting a mass balance on the magnesium, TOC and solids passed through the plant for one month. $MgSO_4 \cdot 7H_2O$ was used to initiate the process in order to

Table 2. Comparison of Color, TOC, and THMFP Removal from Lake Washington Water Via Coagulation. Raw water (Color), TOC, and THMFP was 230 cpu, 31 mg/L, and 600 μg/L.

Coagulant Base	Optimum Dose mg/L as ion	Optimum pH	% Removal Color	% Removal TOC	% Removal THMFP
$Al_2(SO_4)_3 \cdot 18H_2O$	$21(Al^{+3})$	5.5	87	76	59
$Fe_2(SO_4)_3 \cdot XH_2O$	$30(Fe^{+3})$	5.0	84	73	57
$MgSO_4 \cdot 7H_2O$	$31(Mg^{+2})$	11.5	84	64	63

Table 3. Design Table Summary.

Unit	Design Parameters	Comments
Rapid Mix	10-30 seconds	Short rapid mix appears to be desirable in color removal applications.
Flocculation	15-30 minutes	Floc forms rapidly. However, contact time increases color adsorption.
Clarifier	1.0 gpm/sf	The use of polymers prevents excessive $Mg(OH)_2$ floc carry-over.
Filtration	2.0-4.0 gpm/sf	Filter rates up to 4.0 gpm/sf were evaluated in Montgomery. Increased rates improved performance normally.
Settled Water Carbonation	10-30 minutes	Two stage, separated by time shown as design parameters.
Sludge Carbonation		
Purchased 100% CO_2	15 minutes	
Kiln Gas - 18% CO_2	60 minutes	Foaming problems solved by collection in launder drained to tail box.
Sludge Thickening	40-50 lbs/sq.ft./day	Increase in loading rate will produce solids underflow less than 30%.
Sludge Dewatering	25-35 lbs/sq.ft./hr.	Lower rate is for feed solids less than 30%.

Source: "Plant Scale Studies of the Magnesium Carbonate Water Treatment Process," A. P. Black and C. G. Thompson, September 1974, Black, Crow and Eidness Engineers, Inc., Gainesville, Florida.

duplicate the original start up mode and conduct the evaluation as quickly as possible. $MgSO_4 \cdot 7H_2O$ is not required for start up as $Mg(HCO_3)_2$ could be recovered from the $Mg(OH)_2$ sludge but $MgSO_4 \cdot 7H_2O$ allows a more rapid start. The main objectives of this study were to determine if the process could be operated continuously and to find the effect of continuous recycle on finished water quality in the original mode. To accomplish this, flow was monitored and several magnesium, TOC and solids samples were taken at various points in this process to determine material flow and quality, and data was gathered to conduct a basic mass balance on the overall process.

The only way of getting magnesium out of the process was in the finished water or in the sludge produced from vacuum filtration. The lime kiln was not operated during the study because of economics. During the plant recycle study it soon became evident that much more magnesium was being gained from treating the raw water than could be used in the process. The mass transfer of magnesium into and out of the plant is shown in Figure 6. The inputs are the magnesium precipitated from the raw water and the magnesium used for process start up which are denoted as "+Precipitated Magnesium+" and "+Initial Magnesium+" respectively. Approximately 500 to 550 lbs/day of magnesium were precipitated from the raw water and 4300 lbs of magnesium were used for start up. The only expected magnesium loss in the process was in the vacuum filtered solids which was about 100/lbs/day and is denoted as "-Vacuum Filtered Magnesium-" in Figure 6. The $Mg(HCO_3)_2$ coagulant dose as magnesium is not a process output or input and is shown as "Recycled Magnesium" in the lower half of Figure 6. The purpose of Figure 6 is to show that all the magnesium was accounted for during the plant evaluation.

There was 16,000ft^3 of storage cells for the recovered $Mg(HCO_3)_2$. The dissolved $Mg(HCO_3)_2$ could only be concentrated to approximately 5600 mg/L as Mg^{++} because of the equilibrium constant, $10^{-2.4}$, for the recovery reaction given in equation (1). Therefore, the total amount of storage of magnesium as $Mg(HCO_3)_2$ was limited to about 5800 lbs., other than that magnesium could be stored in process in the clarifiers as $Mg(OH)_2$ sludge or to a much lesser degree in the thickener (after magnesium recovery). Less than 1000 lbs of magnesium was retained in the clarifier and thickener so that total storage was less than 6800 lbs. Since an average of 525 lbs/day of magnesium was removed from the raw water, the average residence time that magnesium would

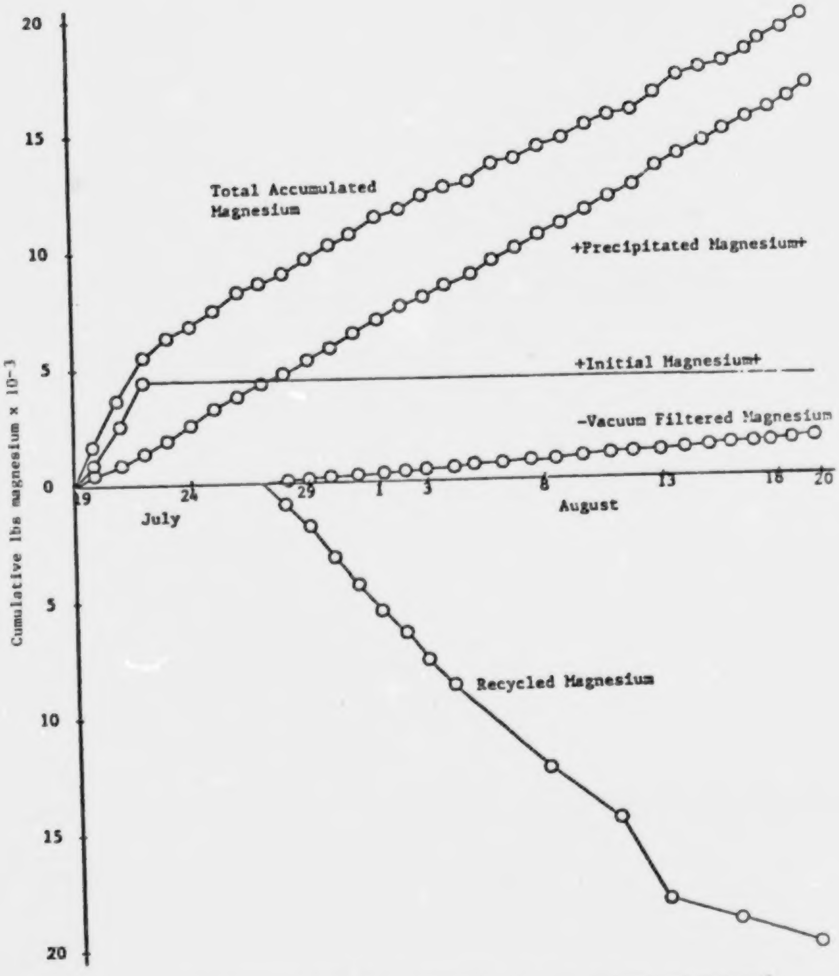


Figure 6. Mass transfer diagram for magnesium inputs, outputs and internal recycle.

spend in the process was about two weeks before $Mg(HCO_3)_2$ liquor had to be wasted. The residence time was reduced to less than one week when the raw water magnesium concentration increased from 5 mg/L to 10 mg/L Mg^{++}.

The number of times the $Mg(HCO_3)_2$ was reused was dependent on the magnesium dosed, the treated flow and the mass of magnesium in storage. For the Melbourne conditions of 10 mg/L $Mg(HCO_3)_2$ as Mg^{++}, 12.8 mg/L and 5800 lbs of $Mg(HCO_3)_2$ as Mg^{++} in storage, 1070 lb/day of $Mg(HCO_3)_2$ as Mg^{++} would have to be dosed for coagulation and 525 lbs/day of $Mg(HCO_3)_2$ as Mg^{++} would have to be wasted. The total magnesium storage (6800 lbs) divided by magnesium dosed (1024 lbs/day) averaged about one week and there was about two weeks of magnesium residence in the process before $Mg(HCO_3)_2$ was wasted. Therefore, the average magnesium reuse under these conditions was twice. The number of magnesium reuses increased directly with coagulant dose and decreased with magnesium concentration in the raw water. Under the normal Melbourne conditions, the maximum number of magnesium reuses would be two.

This is very significant because it dispels any possibility of the $Mg(HCO_3)_2$ liquor becoming infinitely concentrated with organics and contamination of the finished water. During the recycle study at Melbourne, samples were regularly taken from the $Mg(HCO_3)_2$ storage tanks and reused in jar tests. The results are shown in Figure 7 and indicate that using recycled $Mg(HCO_3)_2$ as a coagulant removed more color than lime alone but not as much color as unused magnesium. Importantly this data clearly showed that recycled $Mg(HCO_3)_2$ did not contaminate the finished water with increased organics.

The remaining significant finding from the in-plant studies at Melbourne showed that the solids could only be removed from the process at 2.3 lbs/ft^2-hr by the vacuum filters. The design criteria required 25 to 35 lbs/ft^2-hr through these filters. This low flux rate through the filters was suggested to be caused by either organics, undissolved $Mg(OH)_2$ or alum in the sludge. Vacuum filter rates found at Dallas, Texas (City of Dallas, 1981) in a one-year pilot study of the magnesium process averaged 8.0 lbs/ft^2-hr. These rates are very significant at Melbourne because the process could not be operated continuously due to solids accrual in the system. At Melbourne, as in any closed loop system, solids handling is the key to success and prevented the system from operating properly.

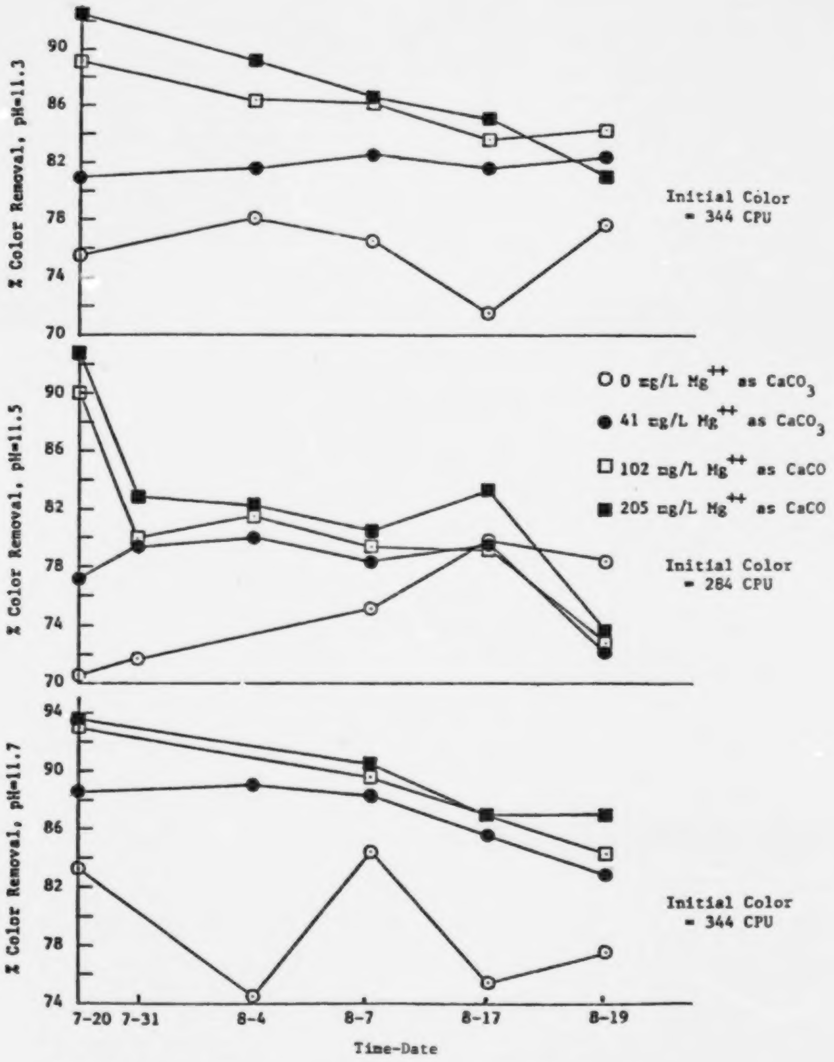
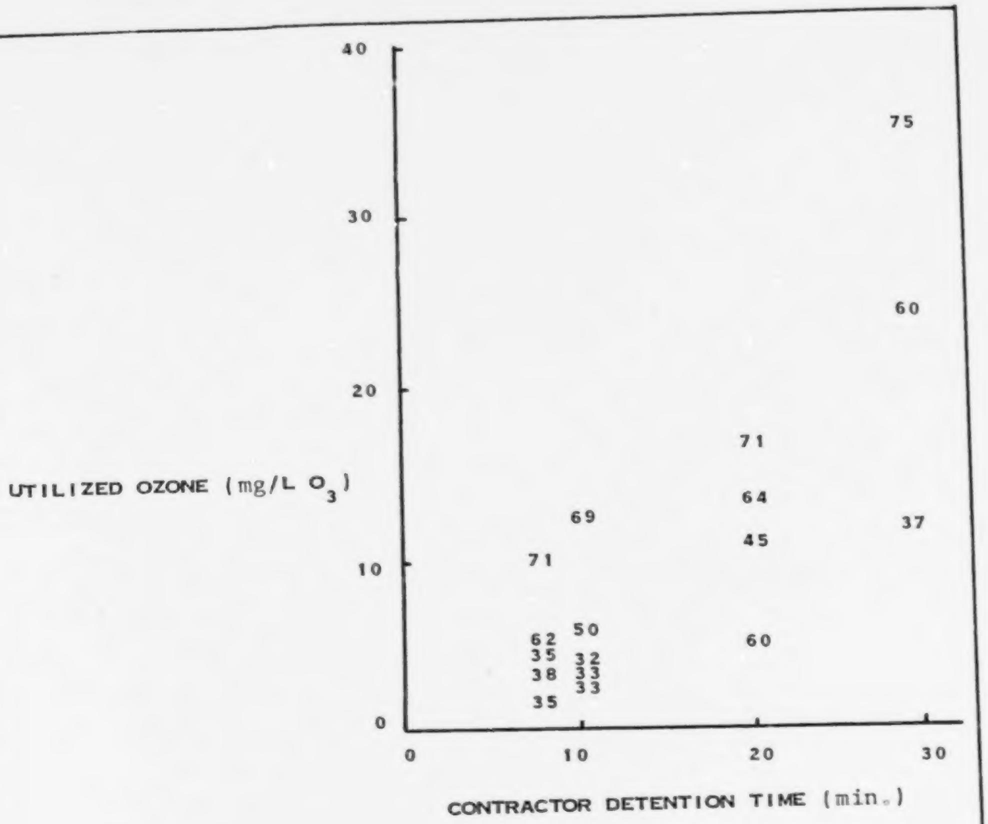


Figure 7. Percent color removal as a function of time for recycled $Mg(HCO_3)_2$ samples at coagulation pH of 11.3, 11.5 and 11.7. 7-20 date represents coagulation with fresh $MgSO_4 \cdot 7H_2O$ which was used for start up. All other dates are time when recovered $Mg(HCO_3)_2$ was taken from process and recycled in jar tests.

This brief history of the magnesium process is important to this study because it does show that 1) the process was implemented prior to the THM regulation, 2) the magnesium used in the process is a function of equilibrium chemistry and process storage, 3) ozone and GAC were not effective in reducing THMFP of the finished water, 4) recycling $Mg(HCO_3)_2$ improves finished water quality, and 5) solids handling is a major problem in this process. These findings will relate to the results described in this report.

Smith and Gillespie Engineers, in cooperation with UCF, also undertook additional work at the Melbourne plant to investigate the possibility of ozonation and air stripping to reduce the THM's in the finished water (Smith and Gillespie, 1982). The intent was to use ozone for removing the color remaining after coagulation followed by chloramines for disinfection. The results of the ozonation studies are shown in Figures 8 and 9. These results indicate 1) that ozone did not remove all of the remaining color, 2) the efficiency of color reduction by ozone varied inversely with the amount of color present and 3) ozonation at Melbourne would be expensive, requiring at least 7 mg/L of utilized ozone to achieve a final color of 15 cpu. The results of the air stripping work are shown in Table 4. These results indicate that not all of the THM's could be removed by tower aeration, because even when the free chlorine was quenched, THM formation continued. This could have possibly resulted from intermediary forms of chlorinated organics that were not volatile, but would become THM's after aeration was complete as the contact time never exceeded five minutes during aeration. Therefore no indication was ever obtained that tower aeration would sufficiently control THM's at air/ water ratios ranging from 10 to 141.

The amount of chlorine required to reduce color to 15 cpu was also investigated in-plant by Smith and Gillespie (S&G, 1982). The results are shown in Table 5 and indicate that THM formation in excess of 100 μg/L would occur for the high chlorine doses required at Melbourne. The final color achieved in these tests was still over 15 cpu and demonstrates the complexity of meeting both a color and THM standard in a highly colored surface water.



NOTES: 1. INFLUENT COLOR VALUES RANGE
FROM 15 TO 25 CPU

FIGURE 8

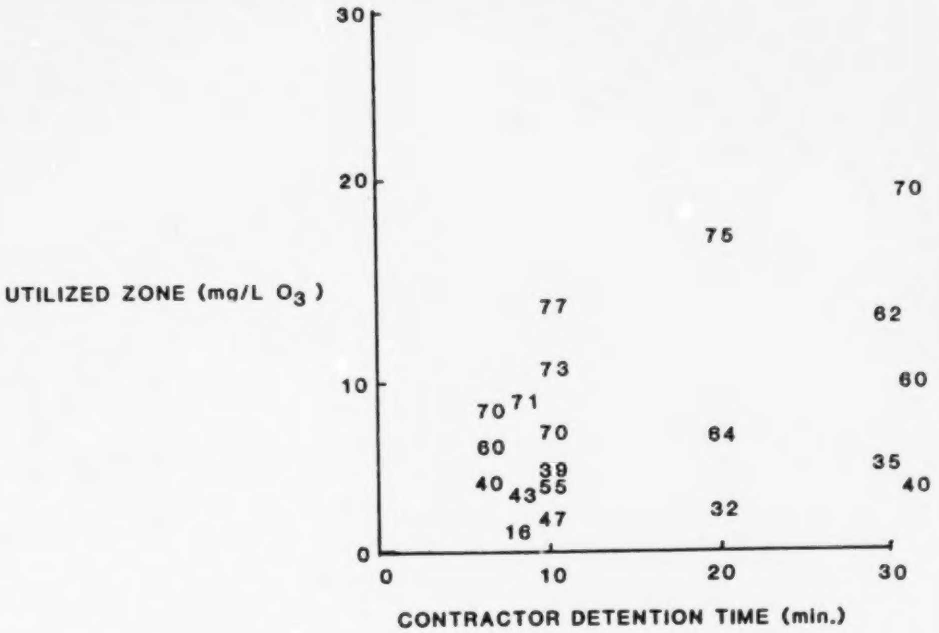
PERCENT COLOR REMOVAL
FROM THE ALUM TREATED EFFLUENT

ENGINEER'S PRELIMINARY REPORT
WATER TREATMENT EVALUATION
THM CONTROL AND PLANT IMPROVEMENTS

MELBOURNE, FLORIDA

SMITH AND GILLESPIE ENGINEERS, INC.
JACKSONVILLE, FLORIDA

PROJECT NO. 7204-08-02 JANUARY 1983



NOTES: Influent color values range from 34 to 44 CPU

FIGURE 9

PERCENT COLOR REMOVAL
FROM THE MAGNESIUM PROCESS EFFLUENT

ENGINEER'S PRELIMINARY REPORT
WATER TREATMENT EVALUATION
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Table 4. Summary of Chemical Doses, Color, and Trihalomethane Data for Air Stripping of the High Color Filter Effluent.

Pilot Plant Flows		Air to Water Ratio	Free Cl_2 Contact time	Chemical Doses (mg/L)		Color (cpu)		Total THM (ug/L)	
Water (GPM)	Air (CFM)	(vol.)	(min.)	Cl_2	NH_3	Filtered Water	Finished Effluent	Before Air Strip.	After Air Strip.
9 Foot Saddle Packing Height									
10.3	194	141	3.6	30	4.3	33	19	196	105
15.8	160	76	4.7	32	8.2	45	27	254	115
25.1	153	46	4.4	18	3.4	41	20	228	130
35.4	120	25	4.2	29	4.4	41	24	210	120
46.1	94.1	15	4.0	20	4.5	44	20	217	144
58.1	78.2	10	3.8	28	7.2	43	22	254	173
12 Foot Saddle Packing Height									
15.7	169	83	4.7	28	4.6	36	21	170	99
25.5	148	43	4.4	34	4.3	45	23	220	115
46.5	104	17	4.0	26	4.4	37	24	188	105
54.9	78.4	11	4.0	25	5.3	41	20	212	114

Table 5. Chlorine Requirements for Trace Color Reduction in the High Color Filter Effluent.

Chlorine Contact Time (min)	Chlorine Dose (mg/L Cl_2)	Cl_2 Residual Following Contact Period (mg/L Cl_2)	Color (cpu) In	Color (cpu) Out	THM Concentrations (μg/L) $CHCl_3$	THM Concentrations (μg/L) Total
3.0	30	23.9	53	24	--	--
6.0	30	25.1	53	21	184	215
12.0	30	18.8	53	20	184	216
12.0	25	13.8	60	29	181	214
17.9	21.5	13.0	60	25	221	259

CHAPTER 5

WATER SUPPLY AND TREATMENT AT MELBOURNE

5.0 Introduction

It is the intent of this chapter to describe the raw water source and the watershed as well as the process and finished water quality at Melbourne. This description is intended to highlight sources of organics in the water supply as well as describe the potable water source at Melbourne.

5.1 Raw Water Source

The upper St. John's River Basin encompasses approximately 1000 square miles of marshland on the east coast of Florida. It contains three lakes: Helen Blazes, Sawgrass and Washington. The latter serves as the raw water source for the City of Melbourne, Florida which serves a total population of approximately 100,000. There is a fourth lake, Blue Cypress, in the upper basin which precedes any of the latter lakes. This lake is located in a watershed that was historically in a natural portion of the total upper St. John's watershed. However, early development in the thirties utilized dikes and canals to remove water from the marsh to provide land for urban and agrarian uses. The current status of the upper St. John's basin is shown in Figure 10. As can be seen, the majority of the drainage in the upper basin involving Lake Blue Cypress is exhausted to the Indian River via the Feldsmeer Canal. A small portion of this drainage passes the Feldsmeer and is eventually available as a raw water source for Melbourne. The quality and quantity of this water is largely unknown. Because of the dike and Feldsmeer Canal, the upper St. John's basin that truly affects Melbourne can be defined as beginning at the Feldsmeer grade and preceding north to Lake Washington.

The extensive diking and canaling practices in this portion of the basin directly affects the quality and quantity of the water in Lake Washington. Foster and Taylor (1978) have shown from existing water quality data that the three lakes in the upper St. John's basin are eutrophic because of the high nutrient loading. Moreover, the uppermost lake, Helen Blazes, which is the

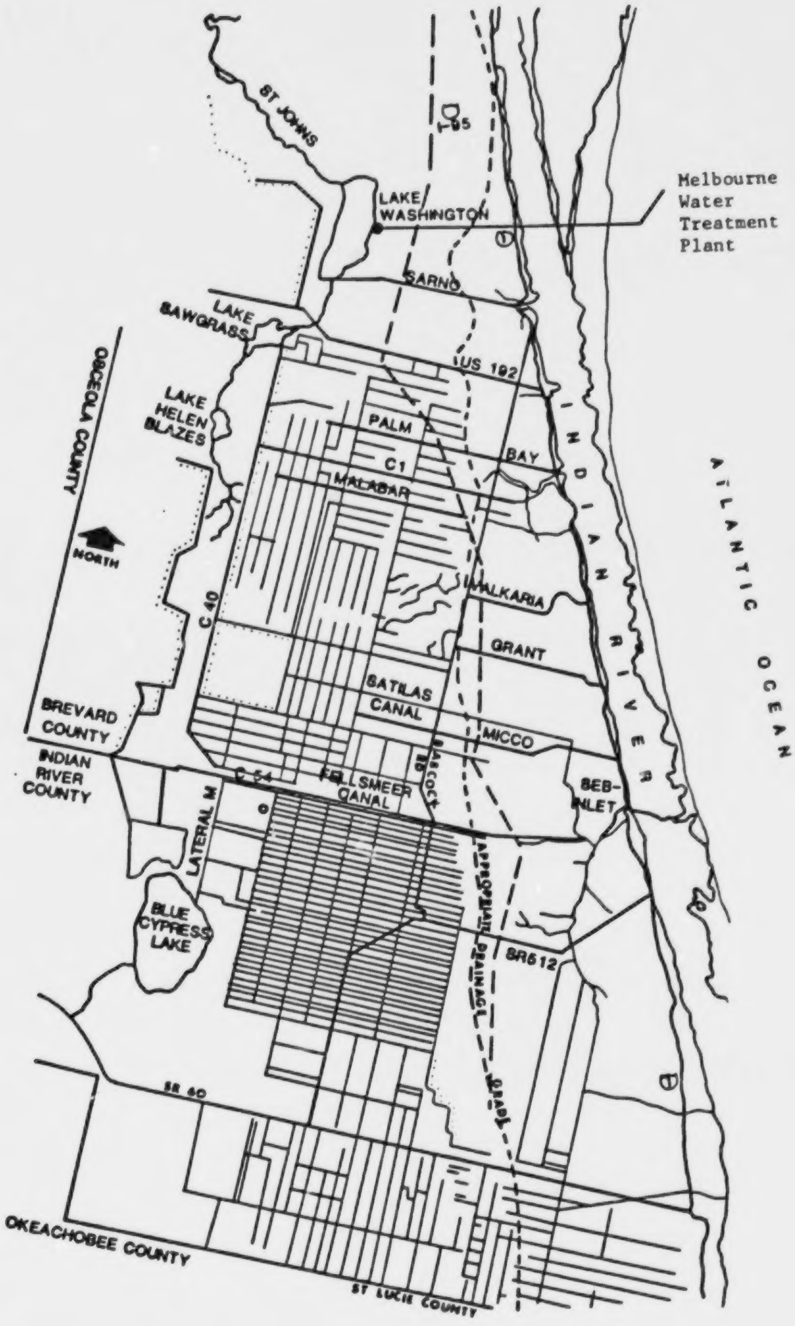

ST JOHNS
I-95
LAKE WASHINGTON
Melbourne Water Treatment Plant
SARNO
LAKE SAWGRASS
US 192
OSCEOLA COUNTY
LAKE HELEN BLAZES
PALM
C1
BAY
MALABAR
NORTH
C40
VALKARIA
GRANT
SATILAS CANAL
MICCO
BREVARD COUNTY
INDIAN RIVER COUNTY
C 54
FELLSMEER CANAL
BABCOCK RD
SEB-INLET
LATERAL M
BLUE CYPRESS LAKE
APPROPRIATE DRAINAGE GRADE
SR512
SR 60
OKEACHOBEE COUNTY
ST LUCIE COUNTY
INDIAN RIVER
ATLANTIC OCEAN

Figure 10. St. Johns River Upper Basin

most severely stressed, initially receives the agricultural drainage made possible by the existing canals. Unless this practice is significantly altered, Foster and Taylor (1978), have projected a future decrease in water quality in Lake Washington.

There are variations in raw water quality due to rainfall. As rainfall increases in the drainage basin of the St. Johns River and the storage capacity of the basin which is marsh land is exceeded, the color of the raw water increases and the chlorides, magnesium, calcium, and alkalinity decreases. Conversely when rainfall decreases, these parameters vary in the opposite manner. During dry periods, Melbourne has a problem with high chlorides and the color is about 50 cpu. During the wet periods, colors of 250 cpu are not uncommon. These variations can be seen in Figure 11. The highest raw water color occurs not necessarily when rainfall or flow is highest but just when the storage capacity of the basin is exceeded and the marsh is first flushed after a long storage period. Such discharges have caused color increases from 50 to 250 cpu in less than one day.

The current water quality of Lake Washington is shown in Figure 11. Significant problems for Melbourne are: 1) increasing chloride content, 2) high THM content in the finished water, 3) a growing distribution system in naturally corrosive environments, and 4) quality and quantity limitations in the raw water source because of the natural peat watershed and the present drainage practices. The nearest alternate raw water source other than Lake Washington is 30 miles away and would cost several million dollars to utilize.

5.2 Process Description

The magnesium carbonate process at Melbourne, Florida is designed to produce 16 mgd of finished water. The process utilizes coagulant recovery and recalcination which eliminates the need for sludge disposal. The flow diagram for the process is shown in Figure 1. There are two main treatment trains for this process, one for water and one for solids. The major unit operations for the water production train are 1) pumping raw water, 2) rapid mix or coagulation, 3) flocculation-sedimentation, 4) recarbonation, 5) filtration, and 6) disinfection. The major unit operations for the solids are 1) rapid mix, 2) flocculation-sedimentation, 3) recarbonation, 4) filtration, 5) magnesium recovery, 6) sludge thickening, 7) vacuum filtration, and 8) recalcination.

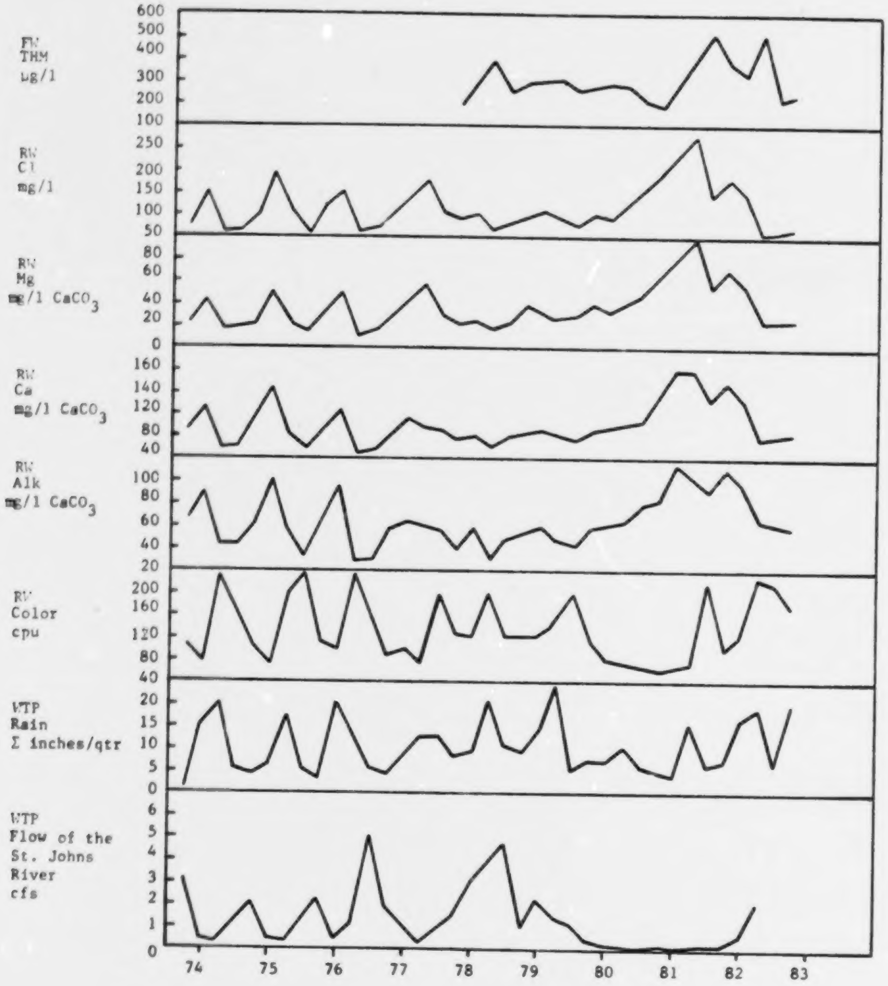


Fig. 11. Finished water (FW) THM, raw water (RW) quality, rainfall and St. Johns River Flow at the Melbourne Water Treatment Plant (WTP).

Pumping from the backwash recovery pond also affects both the liquid and solid treatment trains.

5.2.1 Liquid Train

The raw water is taken from Lake Washington and pumped to rapid mix. The raw and finished water quality during these studies is given in Table 6. Lake Washington is not a good raw water source because of 1) the constantly high TOC concentration, 2) the tendency towards high TDS and chloride concentrations during drought conditions, and 3) the inconsistency of supply and varying quality due to drought conditions and intrabasin activities affecting water quality. The design criteria for the Melbourne plant are shown in Table 3. These criteria were developed from pilot plant studies conducted at Melbourne, Florida and Montgomery, Alabama.

The rapid mix process provides for the addition of polymer, the magnesium bicarbonate ($Mg(HCO_3)_2$) coagulant, lime for pH control, powdered activated carbon (PAC) for taste and odor control and starch as a settling aid, in that order. Alum is used as a polymer at a dose of 20 to 25 mg/L $Al_2(SO_4)_3 \cdot 14H_2O$ and is added before any other chemical to the incoming raw water line, followed by $Mg(HCO_3)_2$ and lime. The $Mg(HCO_3)_2$ and lime doses are a function of the desired coagulant dose and coagulation pH.. The design criteria were a coagulation pH of 11.15 and $Mg(HCO_3)_2$ doses of 145 mg/L and 42 mg/L as $CaCO_3$ for high and low raw water color conditions. Approximately 9 mg/L of PAC and 0.4 mg/L of starch is added to the top of the rapid mix unit in a turbulent zone as the water flows from rapid mix. Rapid mix is conducted in an 8' x 8' x 17.25' chamber in which the water flows from bottom to top. It is mixed by a 10 Hp rapid mixer with two 32" diameter 3-bladed propellers which rotate at 52 to 155 rpm. The detention time in rapid mix is 45 seconds at 16 mgd. Flow is continually monitored into the rapid mix operation. The major products formed in rapid mix are calcium carbonate ($CaCO_3$), magnesium hydroxide ($Mg(OH)_2$) and adsorbed organics which eventually leads to color removal.

The water is passed through manually adjusted gate valves from rapid mix to two separate flocculator-clarifier units. Both clarifiers existed when the plant was converted from alum to $Mg(HCO_3)_2$. The Dorr unit has a separate 65' x 16' x 16' flocculator from the 80' x 80' x 15' rectangular clarifier. The flocculator contains two rotating flocculator blades on 14.3' centers

Table 6. Melbourne Water Treatment Plant Data for 1982.

	Range of Monthly Avgs			Avg. of Monthly Avgs
Raw Water Quality	High	Low		
pH	8.1	7.3		7.6
M. Alk as $CaCO_3$	117	57		83
T. Hardness as $CaCO_3$	261	93		165
Ca Hardness as $CaCO_3$	182	72		122
Mg Hardness as $CaCO_3$	79	20		43
Chlorides	189	55		113
Temperature	85	63	°F	76
Color	254	71	cpu	169
Fl	0.30	0.12		0.19
Fe	0.29	0.06		0.14
TDS	601	227		404
TOC	45	22		36
Finished Water Quality				
pH	7.8	7.6		7.69
p Alk as $CaCO_3$	0	0		0
M-Alk Hardness as $CaCO_3$	102	39		56.5
T Hardness as $CaCO_3$	252	137		188.5
Ca Hardness as $CaCO_3$	242	133		176
Residual Chlorine	8.9	5.8		7.3
Color	7	2	CPU	2.8
Fl	1.04	0.57		0.82
Aluminum	1.37	0.01		0.35
Turb., NTU	4.7	0.67	NTU	1.8
TDS	567	201		416.8
Conductivity	700	326	μmhos/cm^2	495
Chlorides	201	72		128.7
Fe	0	0		0
InstTHM	514	208	μg/L	NA*
Chemicals Used				
Lime	232	27		186
Chorine (post)	26.9	13.5		19.3
Fluorides	0.91	0.59		0.79
Alum	121.6	14.7		38.1
Carbon	10.8	4.6		7.9
CO_2 (100%)	178.2	0		130.9
$Mg(HCO_3)_2$	182	0		NA
Operation time/day	24.0	20.8	hours	22.7
Total Raw Water pumped	12.90	11.23	mgd	12.03
Total Finished water	12.02	10.05	mgd	11.42
Avg. hrs. between filter washings	54.9	21.4	hours	33.7

All data in mg/L unless otherwise specified.

*NA - not applicable, missing some monthly data.

which are 14.5' by 0.5' and rotate at approximately 2 rpm. The Walker unit is circular, has a 90' diameter and has self-contained rapid mix and flocculation units. The detention time in both these units is 2.15 hours at 16 mgd. The design criterion for these units is a maximum surface loading rate, SLR, of 1 g/sf/min. There is no direct measurement of flow from the rapid mix basin to each clarifier. The sludge is pumped from each of the clarifiers to the magnesium recovery operation.

The settled water from each clarifier flows to two identical recarbonation units. The flow into each recarbonation unit passes perpendicularly from a common trough into the two units through manually adjusted gate valves. These valves are equally spaced, two to each recarbonation unit. The recarbonation units are 12' x 20' x 15' in the primary and secondary recarbonation zones which meets the 5-minute detention time design criterion in each zone. The settling zone is 72' x 20' x 15' which meets the 30-minute detention time design criterion at 16 mgd. The pH is reduced to 10.3 in the primary recarbonation zone with CO_2 which forms $CaCO_3$ in the process and passes into the settling zone. The pH is reduced to 8.3 in secondary recarbonation. The settled $CaCO_3$ sludge is either recirculated to the rapid mix unit or primary carbonation zone to provide nuclei for particle growth. Each of the CO_2 reaction zones is baffled to reduce short circuiting.

The treated water passes to dual media (anthracite, sand and gravel) filtration. The plant was designed to chlorinate in the 36" line connecting the secondary recarbonation unit and the filters but was operated using chlorination after filtration to reduce THM's. The design rate for the filters is a maximum of 4 g/sf/min which is achieved at 16 mgd. The filtered water is passed to the wet well or ground storage before distribution. The solids and the water from filter backwash pass to the backwash storage pond where the backwash water is recovered by recycling to the raw water line. The $CaCO_3$ solids in the pond can only be removed by pumping.

5.2.2 Solids Train

The sludge from the clarifiers is measured and pumped to the recovery unit where the $Mg(OH)_2$ solids are solubilized to $Mg(HCO_3)_2$ with CO_2. There are two carbonators that consist of four 6.5' x 6.5' x 6.5' cells where CO_2 is dispersed at the bottom of each cell by a large rotating disk. There is no separation between any of these cells. The design criterion for each of these sludge carbonators is a detention time of 15 minutes if 100% CO_2 gas is used and 60 minutes if kiln gas at 18% CO_2 is used.

The carbonated mixture is passed completely to a 50' diameter thickener which separates the recovered $Mg(HCO_3)_2$ which is soluble from the $CaCO_3$ sludge. The design criterion for the thickener is 40 to 50 lb/sf/hr at continuous operation in order to achieve a solids underflow from the thickener of no less than 30% TSS. The sludge from the thickener goes to the vacuum filters which were designed to operate at a surface loading rate (SLR) of 25 to 35 lb/sf/hr. The lower SLR was specified if the feed solids dropped below 30% TSS. The recovered $Mg(HCO_3)_2$ was passed from the thickener to $Mg(HCO_3)_2$ storage for reuse as the primary coagulant. The lime kiln was designed to convert 2,083 lb/hr of dry solids of which 1,728 were $CaCO_3$ yielding 96-70 lb/hr of CaO. There is no storage between the lime kiln and the thickener. The only accrual of $CaCO_3$ solids to be fed to the kiln is in the thickener.

5.2.3 Process Control

The process was designed to operate under automatic control. That is, proportional, integral and derivative controllers were designed to continuously monitor 1) coagulation pH, 2) primary recarbonation pH, and 3) sludge carbonation pH. From these measurements, 1) the lime feed is controlled to regulate coagulation pH, 2) the CO_2 flow in the recarbonation basin is controlled to regulate primary and secondary recarbonation pH, and 3) the CO_2 flow into the sludge carbonator is controlled to regulate the pH in the recovery unit which controls magnesium recovery. The $Mg(HCO_3)_2$ flow rate from storage is regulated by flow monitoring. The filters are constant rate and are automatically controlled. There are other controlled variables in the process that are manually controlled such as chlorine, polymers, PAC, hexametaphosphate and fluoride. However, the three controls previously mentioned are the keys to solids production, $Mg(HCO_3)_2$ coagulation and recovery which are the major factors of these processes. There are several controls for the operation of the kiln; however, evaluation of the kiln operation was not a part of these studies.

5.2.4 Process Comments

The $Mg(HCO_3)_2$ process has the distinct advantage that no sludge disposal is required. To achieve this an automatically controlled, closed loop plant was constructed which utilized magnesium recovery by carbonation and lime recovery by recalcination. This process requires awareness of mass transfer and storage while operation is ongoing. It is more complex than a conventional process where sludge is discharged to a series of beds and is then usually taken to a land fill or other means of final disposal. This process has a disadvantage in that its successful operation requires technical knowledge and a degree of supervision that is uncommon in typical water treatment plants.

Chlorination serves two purposes in this process. Chlorination serves as the means of providing a disinfecting residual and as the means of removing the color remaining after coagulation. This was standard engineering practice prior to the mid-seventies when the trihalomethane (THM) regulation was proposed and finally adopted. This process, as any conventional process would in an identical situation using chlorination, produces THM's in excess of the 0.1 mg/L regulation. Melbourne, under the previous alum process, had the highest InstTHM concentration recorded by EPA in a nationwide survey in the late seventies (NOMS, unpublished). THM's were not considered as original design criteria but are a current problem. Therefore, the plant cannot be operated as designed and meet regulations since design and construction were completed before the THM regulation was implemented.

5.2.5 Finished Water Quality

The 1982 average monthly finished water quality is shown in Table 6 in addition to the average monthly chemical doses and raw water quality. The only constant problem was the high InstTHM concentration in the finished water. The THM values shown in Table 6 are in-plant THM's. These are typically above 200 µg/L and at times have reached 1200 µg/L in the distribution system. During low flow conditions in the dry period chloride concentrations have approached 300 mg/L but not consistently. The only other problem at Melbourne has been the maintenance of a chlorine residual in the distribution system during summertime conditions. The absence of a residual has permitted high bacterial growth and caused some taste and odor complaints.

CHAPTER 6

EXPERIMENTAL METHODS AND QUALITY CONTROL

6.0 Introduction

This section will present the field and laboratory procedures followed in performing the various phases of the project. Descriptions of the individual phases are presented elsewhere.

Field procedures included gathering data on temperature, dissolved oxygen, pH, flow rate and disinfectant residuals. In addition to obtaining and recording these data, water samples were taken at various points in the treatment process and distribution system. In all cases, analytical procedures utilized were those described in Methods for the Examination of Water and Wastes (U.S. EPA, 1979) or Standard Methods for the Examination of Water and Wastewater, 15th ed. (APHA, 1980).

Laboratory analyses included TOC, inorganic carbon, pH, temperature, color, total chlorine residual, free available chlorine, combined (mono and dichloramine) chlorine, chlorine dioxide, chlorite, chlorate, chloride, ozone, trihalomethanes, and trihalomethane formation potential.

Quality assurance procedures were followed for parameters tested on a routine basis. These procedures included replicate analyses, spikes and participation in EPA Performance Evaluations. Laboratory analyses for most parameters were performed at the University of Central Florida College of Engineering in the Department of Civil Engineering and Environmental Sciences Laboratories. Analysts were either members of the UCF staff or graduate students in the environmental engineering program.

Alternatively some tests were performed at the Melbourne South Water Treatment Plant. These included routine monitoring of water temperature, pH, color and standard plate count in the GAC column systems. Members of the plant staff were responsible for collecting samples and analyzing these parameters on a regular basis, as well as maintaining operation of the column systems including their pumps, chemical feed, ozone generation, etc. A log of their activities was maintained at the plant by all operators and technicians involved with the project.

6.1 Laboratory Procedures

Analytical procedures utilized in the laboratory are listed in Table 7 with corresponding Standard Method number or other reference. Where possible, Standard Methods procedures or EPA approved procedures were followed. Where non-standard methods were employed, tests were conducted to assure the applicability of the method utilized. All methods utilized are discussed separately and in detail below.

One of the most commonly performed procedures in this task was the application of disinfectant to various water samples. These included chlorine, chloramine, chlorine dioxide and ozone. Chlorine was applied as a concentrated stock solution. This solution was prepared by acidifying a saturated solution of calcium hypochlorite ($Ca(OCl)_2$) to pH = 2 with concentrated H_2SO_4. The supernatant was stored in an amber Pyrex glass bottle at 4°C. The concentration of this solution was typically about 4 mg Cl/mL. This solution was standardized before each use by diluting 1 mL to 1 L with distilled water and analyzing for free available chlorine.

Chlorine dioxide was generated using the procedure found in Standard Methods (410A). ClO_2 gas was generated by slowly adding H_2SO_4 to a 25% solution of $NaClO_2$. The gas thus produced was purged from aqueous solution by passing a stream of air through the solution. This stream was bubbled through a second container of acid and finally to a flask containing cold (4°C) distilled water. (See Figure 12.)

The concentrated ClO_2 solution was stored at 4°C in an amber Pyrex bottle and standardized before each use by analytical procedures outlined below. The concentration of this stock solution was typically about 0.2 → 1.0 mg/mL as ClO_2. The solution was used for one month after which any unused portion was discarded. ClO_2 was applied by adding an appropriate amount of the stock to the sample in order to yield the desired dose.

A chloramine stock solution was prepared by dissolving 3.77 g NH_4Cl in 200 mL of distilled water and adjusting the pH to 7.5 using concentrated NH_4OH. Next, 0.67 g calcium hypochlorite ($Ca(OCl)_2$) was dissolved in the ammonia buffer and the final pH adjusted to 9.0 with concentrated NH_4OH. The concentration of monochloramine in the resulting stock solution was

Table 7. Summary of Analytical Procedures.

Procedure	Description	Reference
1. chlorine residuals	Amperometric titration DPD ferrous titrimetric	SM-408C SM-408D
2. chlorine dioxide	Amperometric titration DPD titration	SM-410B SM-410C
3. dissolved oxygen	membrane electrode	SM-421F
4. hardness, total	EDTA titration	SM-314B
Ca^{++}		SM-311C
Mg^{++}		SM-318C
5. pH		SM-423
6. Total organic carbon	oxidation to CO_2, reduction to CH_4, FID	SM-505
7. inorganic carbon		SM-505
8. Standard plate count		SM-907
9. Color	Absorption @ 460 nm	text
10. THM	liq-liq extraction	text
11. THMFP		text
12. Ozone	Amperometric titration	text

SM = 15th Edition of Standard Methods

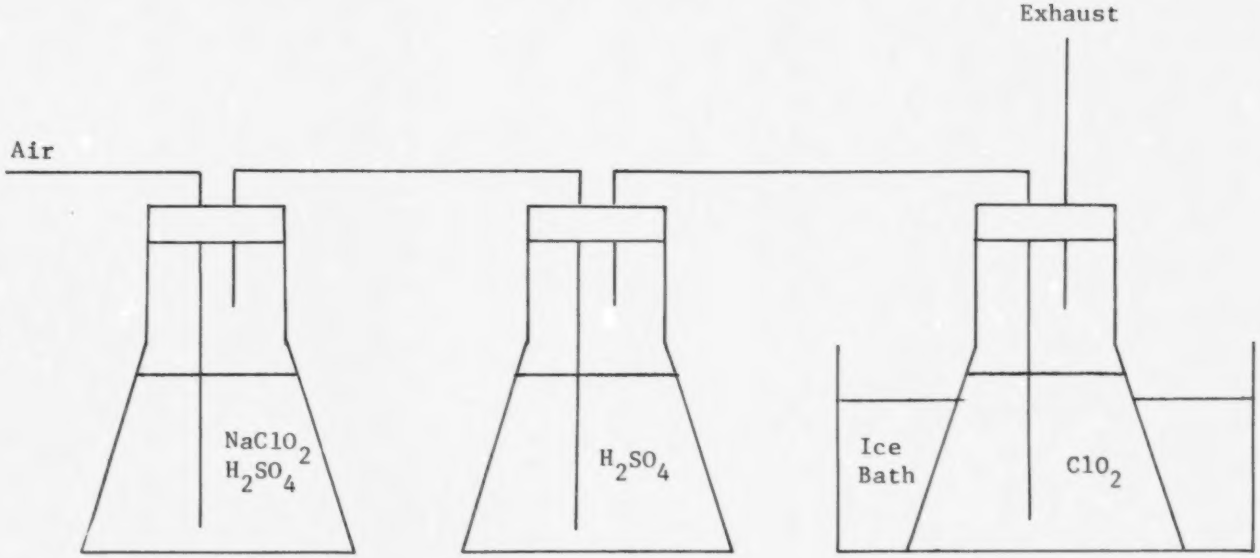

Exhaust
Air
NaClO$_2$
H$_2$SO$_4$
H$_2$SO$_4$
Ice
Bath
ClO$_2$

Fig. 12. Apparatus for ClO_2 generation.

approximately 0.4 mg Cl/mL. The solution was standardized before each use. Degradation of the stock solution occurred over about one month, after which any remaining stock was discarded and a new stock solution prepared.

Ozone was generated in the laboratory by passing a stream of pure, dry air through an electrical discharge ozone generator (Scientific Industries of California, Garden Grove, CA). The amount of O_3 generated was determined by passing the stream of air through a 5% KI solution in a Greenberg impinger. Ozone applied to an aqueous sample was measured indirectly by determining O_3 in the off gas and subtracting from the O_3 generation rate. These measurements were similar in nature to the O_3 calibration measurements made at the Melbourne plant.

Samples of finished and raw water were routinely collected from the Melbourne Water Treatment Plant. Raw water was obtained from the raw water intake pipe running to the plant from Lake Washington. Finished water was taken from a point in the treatment system immediately following filtration but preceding the point of post-filtration pH adjustment and chlorine addition.

Samples were brought to UCF on a weekly basis. The samples were collected and stored in polyethylene-lined 55-gallon steel drums. Water quality data were obtained for each sample when it was taken and again one week later when it was discarded.

All glassware utilized for analytical work was thoroughly washed in warm water with phosphate free detergent, rinsed repeatedly with tap water, and at least three times with distilled water. In addition, Borosilicate glassware used for sample storage and for THMFP or TOC analyses was heated to 500°C for thirty minutes to remove trace organic contaminants. Volumetric glassware was heated only to 350°C to avoid possible deformation.

6.2 Field Measurements

Field measurements were performed at the Melbourne Water Treatment Plant and the surrounding distribution system by project and plant personnel. These included measuring temperature, pH, color, chlorine residual and standard plate count, as well as calibrating ClO_2 and O_3 generating equipment and measuring flows. Plant personnel included licensed operators and laboratory technicians. All of the methods employed at the plant and in the field were identical to those employed at the UCF laboratories except as noted here.

Color at the plant was measured using a visual comparator disc (Hach Chemical Co.). Treatment plant personnel did not regularly adjust pH before measuring color, and, therefore, separate measurements were routinely performed at UCF. Flow rates were measured by timing the flow of a measured volume of fluid. Flow rates were measured regularly on the GAC column systems and the ClO_2 feed system.

Ozone for the GAC system was generated with a Welsbach water-cooled ozone generator. The settings used were 75 volts and 0.5 L/min air flow rate. These values gave consistent performance and generation rate. The ozone generated was applied in a baffled, plexiglass, contact chamber (see Figure 13). The chamber had a hydraulic residence time of approximately thirty minutes. Water was fed to the chamber through a teflon line entering the first baffle compartment in the contact chamber. The water was drawn from a point in the treatment system after filtration but before post-filtration pH adjustment and chlorination.

The performance of the GAC ozone system was evaluated by completing an ozone mass balance. The rate of ozone application was measured at point 1 in Figure 13 immediately upstream of the contact chamber. The rate of ozone escaping with the off gas was measured at point 2. The difference between these two measurements gives the rate at which ozone was dissolved in the water. This rate, divided by the flow rate of water through the contact chambers gives the ozone dose to the water.

$$\frac{\frac{dO_3}{dt}_{in} - \frac{dO_3}{dt}_{out}}{d\,\frac{H_2O}{dt}} = \frac{dO_3}{dH_2O}$$

The dissolved ozone concentration was also measured in contact chamber effluent point 3 in Figure 13. The difference between the concentration calculated in equation 1 and the effluent concentration then gives the amount of ozone utilized per liter of water in the contact chamber. The results of the mass balance are given in Table 8.

Ozone concentration in the treated effluent was also measured on several occasions. These measurements are given in Table 9. These ranged from 0.32 to 0.86 mg/L.

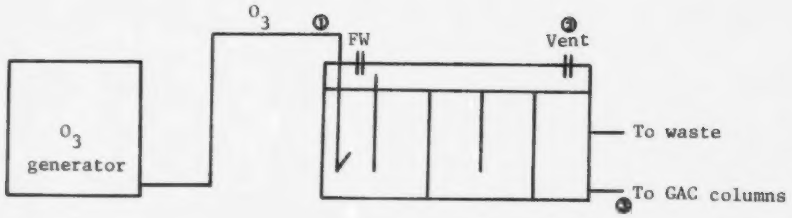

O_3 generator
O_3
①
FW
Vent
To waste
To GAC columns

Fig. 13. GAC-ozone contacting system.

Table 8. Ozone Mass Balance.

O_3 applied (pt. 1) mg/min	O_3 exhausted (pt. 2) mg/min	Flow Rate L/min	O_3 Dose mg/L
7.0	5.1	2.1	0.9
7.2	5.4	1.8	1.0

Table 9. Typical Ozone Concentrations in the Contact Chamber Effluent.

Date	Effluent O_3 (mg/L)
1/83	0.32
3/83	0.75
5/83	0.86
7/83	0.45

These data indicate that approximately 30 percent of the applied ozone actually dissolved in the water. The remaining 70 percent escaped with the off gases. The ozone concentration in the contact chamber effluent varied from approximately 0.3 to 0.9 mg/L. Thus, of that 30 percent of the applied ozone which dissolved in the water, only about 50 percent had reacted after thirty minutes. The total amount of ozone actually undergoing reduction in the contact chamber was therefore on the average 0.5 mg/L. Ozone was never detected in the effluent of the carbon columns, indicating that any dissolved ozone not remaining after the contact chambers was completely consumed in the columns.

Calibration of the GAC-ClO_2 system was performed regularly as the ClO_2 stock solution varied in concentration with time. The ClO_2 stock solution was generated as described above. The ClO_2 stock solution was kept in a refrigerator and fed to the GAC system via a peristaltic pump. The flow rate of the stock solution to the column was calculated using:

$$\frac{\text{mL}}{\text{min}} = \frac{(2\text{mg/L})\ (\text{Total flow L/min})}{(\text{Stock Concentration mg/mL})}$$

where 2 mg/L was the desired ClO_2 dose, total flow was the total filtered water flow through the system and stock concentration was the concentration of the ClO_2 stock solution in mg/mL.

Typically, the ClO_2 concentration ranged from 100 to 400 mg/L, and the flow rate through the system was 1.0 L/minute, so the ClO_2 feed rate was between 5.0 and 20.0 mL/minute. ClO_2 in the stock solution was measured immediately upstream of the ClO_2 contact chamber, so any loss of ClO_2 in the pump tubing was already discounted in the measurement. Since the ClO_2 stock solution concentration varied with time, ClO_2 was measured and the feed rate was adjusted daily.

6.3 Test Description

This section describes in detail the test procedures followed in the analysis of water samples.

6.3.1 Chlorine Residual

Free and combined chlorine residuals were routinely determined using the DPD Ferrous Titrametric Method (method 408D, Standard Methods 1980). In this procedure free chlorine residual is reduced by ferrous titration to a DPD endpoint. Combined residuals are converted to free iodine which is also measured by ferrous titration. The ferrous titrant was standardized weekly against primary standard grade potassium dichromate.

Alternatively, chlorine residuals were measured by titration with standard phenylarsine oxide to an amperometric endpoint (method 408C, 15th ed. Standard Methods, 1980). In this method, as in the DPD method, free chlorine is titrated directly, and combined chlorine forms reacted with iodide ion to form iodine which is measured by the same procedure as free chlorine.

6.3.2 Chlorine Dioxide

Chlorine dioxide was measured by ferrous titration to a DPD endpoint (method 410C, 15th ed. Standard Methods, 1980). This procedure is related to the DPD method for determining chlorine residual and can also be used to differentiate chlorite (ClO_2^-). When free chlorine was potentially present in the sample, it was converted and neutralized by adding glycine to the sample. Alternatively, an amperometric titration procedure (method 410C, Standard Methods, 1980) similar to that used for chlorine residual was employed.

6.3.3 Color

Color was determined by measuring absorbance at 460 nm. Water samples were filtered through a glass fiber filter (Whatman GF/A) and their pH adjusted to 7.6 using concentrated acid or base as needed. The measured absorbance was compared with that of a standard curve of absorbance versus concentration for a series of known chloroplatinate solutions.

Since the method utilized for color measurements was not a standard method, results were compared with those of Standard methods for nine samples. The methods chosen for comparison were the visual comparison method (204 A. Standard Methods, 15th ed.; Method 110.2 U.S. EPA 1979) and the spectrophotometric method (204 B, Standard Methods, 15th ed.; Method 110.3 U.S. EPA 1979).

In the visual comparison method, samples are compared visually to platinum-cobalt color standards of varying concentration. Samples were filtered before comparison to remove turbidity. The pH was then adjusted to 7.6 using concentrated sulfuric acid or sodium hydroxide as needed. The samples were then placed in 50 mL Nessler tubes and matched to platinum-cobalt standards in separate Nessler tubes. The results of the visual comparison method are directly comparable to the method used for this project, since both report results as chloroplatinate units (cpu). The results of the nine measurements are shown in Table 10 and Figure 14. The correlation between the visual comparison method and measuring absorbance at 450 nm was high for the range 0-55 cpu. The relationship between absorbance at 460 m and color concentration was found to be linear between 0 and 500 cpu. Samples with color greater than 200 cpu were diluted with distilled water and remeasured.

The same samples were also analyzed using the spectrophotometric method. This procedure characterizes the color in natural waters in terms of three properties: hue (designated by dominant wavelength), luminance or degree of brightness, and purity or saturation. The last two properties are expressed as a percentage. These properties are determined by measuring the percent transmittance of the sample at a number of different wavelengths. Values for dominant wavelength, luminance, and purity are calculated using equations and diagrams described in Standard Methods. The results obtained using this method are not directly comparable to those found using the other two methods compared in Table 10. The results in Table 10 do indicate that the water samples tested were uniform in the qualitative characteristic of dominant wavelength, with all of the Melbourne samples falling in the range of 570 to 585 nm. This represents hues ranging from greenish yellow to yellowish orange (Standard Methods, 15th ed; 1980 p. 66). The two samples with dominant hue outside of the 570-585 nm range were from sources other than the Melbourne system. Sample 4 was from the UCF potable water system and sample 5 was from the Hillsbourough River.

6.3.4 Hardness

Calcium and magnesium hardness were measured by EDTA titration. Total hardness was measured at pH 10 by titration to an Eriochrome Black T (EBT) endpoint (method 314B, 15th ed. Standard Methods, 1980). Calcium hardness was measured at pH 12 by titration to a murexide endpoint (method 311C, 15th ed. Standard Methods, 1980). Magnesium hardness was determined by difference (method 318C, 15th ed. Standard Methods).

6.3.5 Oxygen

Dissolved oxygen was measured using a YSI membrane electrode dissolved oxygen meter (method 421F, Standard Methods, 1980). The meter was calibrated either in air or a distilled water sample saturated with air. Samples for D.O. analysis were collected in BOD bottles by allowing the sample to flow through a flexible polyethylene tube into the bottle. The sample stream

Table 10. Comparison of Color Results for Different Measurement Methods.

	Method				
	Absorbance @ 460 nm	Visual (Standard Method 204.A)	Spectrophotometric Standard Method 204.B		
Sample	(cpu)	(cpu)	Percent Purity	Percent Luminance	Dominant Wavelength (nm)
1	53	55	6	95.9	575
2	15	14	0	99.7	580
3	10	9	0	99.1	585
4	2	2	0	99.7	500
5	34	35	2	96.8	620
6	10	10	0	99.2	575
7	48	50	5	94.4	574
8	43	45	4	96.7	574
9	11	12	0	95.5	571

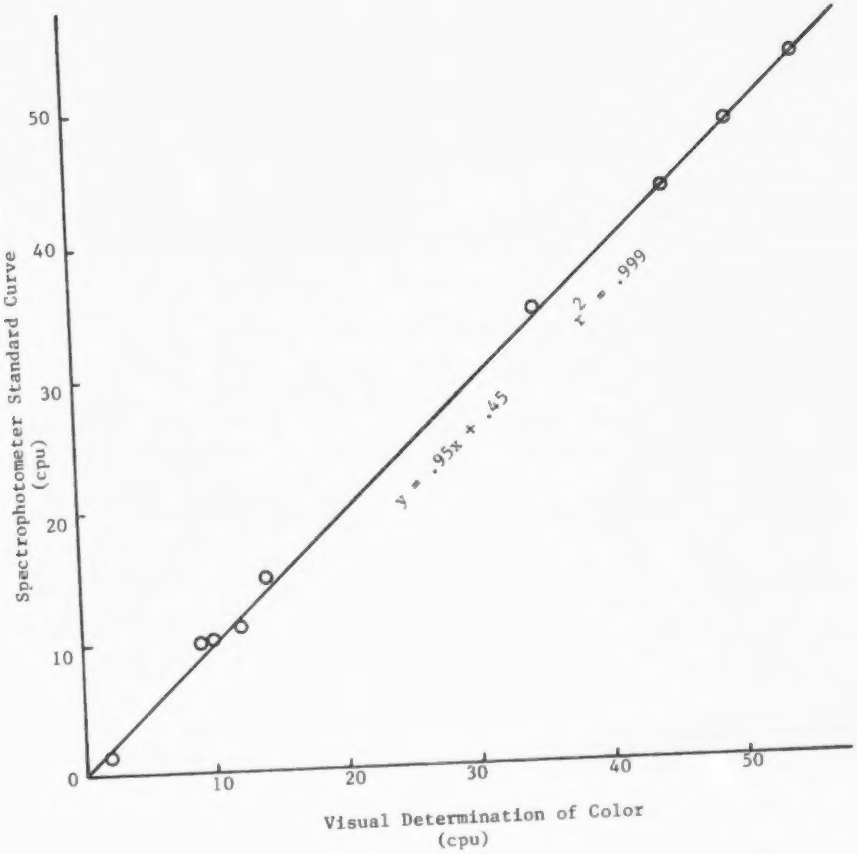


Fig. 14. Comparison of color results using the Visual Color Determination Method (method 204A, Standard Methods, 1980) with results obtained measuring absorbence at 460 nm.

flowed to the bottom of the BOD bottle and the bottle was allowed to overflow. The volume of the overflow was approximately 3 to 5 times the volume of the bottle. At this point the calibrated D.O. probe was added to the bottle and D.O. immediately measured.

6.3.6 Ozone

Ozone was measured in the gas phase and in the dissolved aqueous phase. Both measurements are based on the oxidation of iodide ion to iodide by ozone.

$$O_3 + 2I^- + H_2O \rightarrow O_2 + I_2 + 2OH^-$$

For gaseous measurements, a known volume of the gas stream is passed through a neutral 5 percent KI solution. For dissolved ozone measurements, the KI solution added to the aqueous sample along with a bicarbonate buffer (pH = 8.3). In either case, the iodine formed is titrated with phenyl arsine oxide titrant.

$$I_2 + As^{+3} \rightarrow 2I^- + As^{+5}$$

The endpoint is determined amperometrically to avoid interference common with colormetric indicator.

6.3.7 Standard Plate Count

Microbiological water quality was measured by standard plate count (APHA, 1980 Method 907). This procedure gives a standardized procedure for measuring viable aerobic and facultative anaerobic heterotrophic bacteria. Samples were collected in sterile containers and analyzed within six hours. Appropriate dilutions of each sample were made with sterile Standard Plate Count Agar (American Scientific Products) and plated out on sterile petri dishes. These were incubated for 48 hours at 35°C at which time the number of colonies was counted and results reported as number of colony-forming units/L.

6.3.8 Total Organic Carbon (TOC)

Total organic carbon was measured using a Dohrmann (Model DC-54) TOC Analyzer. This instrument operates by oxidizing organic carbon to CO_2 using exposure to UV light and acidic persulfate solution. CO_2 thus produced is catalytically reduced to methane and quantified using a flame ionization detector. Samples were collected in Pyrex glass bottles with teflon-lined caps, stored at 4°C, and analyzed within seven days of collection.

A TOC stock solution was prepared by dissolving 0.2125 g of potassium acid phthalate in 90 mL of reagent grade water, acidifying with 1 mL concentrated phosphoric acid and diluting to 100 mL. This stock solution contained

1000 mg organic C/L. The stock was stored at 4°C for no more than two months, when it was discarded and a new stock solution prepared.

To standardize the TOC analyzer, a 10 mg/L standard solution was prepared by diluting 1.00 mL of the stock solution to 100 mL using reagent grade water. This standard was analyzed and the instrument output adjusted to 10.000 mg/L plus the output of a blank solution. The detailed procedure for calibrating the TOC analyzer is described in the operating manual for the Dohrmann DC-54 TOC analyzer (Dohrmann DC-54 Manual, Santa Clara, CA).

Samples were filtered through a Wickham GF/A glass fiber filter and diluted with reagent water to a final concentration between 1 and 10 mg/L if the undiluted concentration was greater than 10 mg/L. Each sample was run a minimum of two times. If carryover from the previous sample was evident (i.e., the duplicate analyses differed by more than 10%) the sample was run again until repeatable results were obtained. All results are reported as averages of replicate analysis after correction for any TOC in the dilution water and carryover effects. The correction for organic carbon in the dilution water was to subtract the value of the blank from the analyzed value. Carryover effects were recognizable when two sequential samples had sizeable differences in TOC value. In such a case, the first replicate analysis of the second sample was influenced by the preceding sample. In such cases the first replicate value was discarded and a third or even fourth replicate analyzed to insure the precision of the subsequent replicate analysis.

Inorganic carbon was measured on a Beckman 915B carbon analyzer equipped with an infrared CO_2 detector. A sample of 0.2 mL volume was injected into a catalytic column which converted any inorganic carbon forms to CO_2 which was then quantified by absorption of infrared light (method 505, Standard Methods, 1980).

6.3.9 Trihalomethanes

Trihalomethanes (THM's) were concentrated from aqueous solution by liquid-liquid extraction using hexane as the organic phase solvent (Supplement to the 15th Ed. of Standard Methods Selected Analytical Methods Approved and Cited by the United States Environmental Protection Agency). Ten mL of the sample to be analyzed were carefully measured into a Pyrex test tube containing 2 mL of Nanograde quality hexane. The tube was closed with a one-inch square piece of aluminum foil and a screw cap lid. The mixture was vigorously shaken for 30 seconds and the two phases allowed to separate. Three µL of the organic phase was used for analysis. The operating parameters for the gas chromatographic system are given in Table 11. Chloroform ($CHCl_3$), bromodichloromethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$) and bromoform ($CHBr_3$) were identified and quantified by comparison to standard solutions. Samples outside of the linear range were reanalyzed after dilution of a fresh sample. THM standard solutions were prepared by diluting a stock solution, containing 200 mg/L each of chloroform, bromodichloromethane, dibromochloromethane and bromoform in methanol, in reagent grade distilled water. The 200 mg/L stock solution was obtained in 1 mL ampules (Part #4-8746) from Supelco Inc. (NY).

6.3.10 Trihalomethane Formation Potential (THMFP)

THMFP was measured by adding sufficient chlorine to water samples at pH 7.6 so that a detectable free residual was maintained for 48 hours (unless some other time period was specified). After the incubation period, the chlorine residual remaining was neutralized by adding excess sodium thiosulfate. THMFP in this work was identical to terminal THM's since there was never any THM found in laboratory samples prior to chlorination.

A 250 mL aliquot of the sample was placed in a beaker and the appropriate volume of chlorine stock solution added to produce a dose of 20 mgCl/L. (Raw water samples were chlorinated with higher doses (40-60 mg/L) depending on the nature of the sample, in order to maintain a free residual throughout the incubation period.) Immediately after chlorine addition, the pH was adjusted to 7.6 using concentrated NaOH or H_2SO_4 as necessary. The chlorinated sample was then poured into a 125 mL amber Pyrex glass bottle and fitted with a teflon-lined cap. After the incubation period, usually 48 hours, 1 mL of 0.1N $Na_2S_2O_3$ was added to neutralize the chlorine. Samples were stored in the same bottle at 4°C until analyzed. Analysis was usually completed within two weeks.

6.4 Quality Control

During the initial phases of the project, various measurements were taken to insure analytical precision and accuracy. These measures included strict adherence to analytical procedures described above, careful cleaning of all glassware, proper collection and storage of samples, regular maintenance of analytical equipment and data collection for quality control purposes. This data gathering included the analysis of replicate samples, analysis of spiked samples, and participation in EPA Performance Evaluations. Initial data were

Table 11. Gas Chromatographic System and Operating Parameters.

Model	Hewlett-Packard Model 5750
Detector	Ni^{63} Electron Capture
Detector Temp	210°C
Carrier	5% Methane in Argon
Carrier rate	40 cc/min
Purge	5% Methane in Argon
Purge rate	120 cc/min
Column	6 ft Pyrex 3% SP-1000 on Supelcoport 120/100
Column temp	80°C

utilized to establish quality control limits for continuous monitoring of analytical precision and accuracy. Subsequent quality control data compared to these limits included the analysis of spikes, replicates and participation in EPA Performance Evaluations.

6.4.1 THMFP

Precision refers to reproducibility among replicate observations. During the initial phases, a total of 42 sets of duplicates were analyzed and the range of the duplicates compared to the average and expressed as a percentage, i.e., $|x_1 - x_2|/\frac{1}{2}(x_1 + x_2)$. These data are given in Table 12 for 1981. A large range of values were analyzed (approximately 70 μg/L - 50,000 μg/L). The average percent difference was found to be 6.6% and the standard deviation, 7.6%. Out of the 42 sets of duplicate analyses, the range exceeded 20% of the mean in two cases or 4.8% of the time. Therefore, about 95% of the time, the range of duplicate analyses was less than 20% of the mean. In approximately 75% of the duplicate analyses, the range was less than 10% of the mean value. For continuous quality control, 20% of the mean was chosen as the limit for acceptable difference between duplicate analyses. Any duplicate samples exceeding this limit were reanalyzed and an attempt made to uncover the reason for the variation.

To confirm the initial values, 32 sets of duplicates were analyzed in 1982. These data are given in Table 13 for the first quarter of 1982. The average percent difference for this sample set was 6.0% and the standard deviation of the percent differences 8.6%. The 20% limit was exceeded in two samples or 6.3% of the time. In one case the samples were of fairly low concentration (approximately 40 μg/L) so a relatively small difference resulted in a large percentage difference. In the second case, the samples were of relatively high concentration (approximately 1700 μg/L) and the error was probably due to dilution error. The 10% error level was exceeded only 16% of the time in this set of samples. These data confirmed the choice of limits made in the first data set.

Duplicate samples were measured frequently in all subsequent analytical runs. These data are summarized in Table 14 for the remainder of the project. The majority of the percent differences were below the limit of 20%, with only 6 of 61 differences between duplicate analyses exceeding the 20% limit. All of these instances occurred during or after the fourth quarter of 1982. The

Table 12. Trihalomethane Formation Potential Precision for 1981.

1st Value (μg/L)	2nd Value (μg/L)	% Difference
1223	1321	7.7
1580	1546	2.2
945	956	1.2
523	573	9.1
657	605	8.2
807	754	6.8
930	768	19.1
289	289	0.0
985	1020	3.5
847	710	17.6
534	531	0.6
607	418	36.9
597	594	0.5
873	900	3.0
1031	1009	2.2
504	545	7.8
462	487	5.3
537	474	12.5
968	968	0.0
33800	33800	0.0
47630	47900	0.6
1084	1084	0.0
45500	44400	2.4
1050	1160	10.0
631	631	0.0
680	723	6.1
674	720	6.6
1110	1110	0.0
42600	42600	0.0
41100	43900	6.6
1040	930	11.2
1120	1050	6.5
1040	1040	0.0
1350	1350	0.0
109	104	4.7
128	137	6.8
269	233	14.3
97	85	13.2
151	167	10.1
137	152	10.4
372	376	1.1
73	93	24.1

$n = 42$

$\bar{x} = 6.6$
$s = 7.6$

Table 13. Trihalomethane Formation Potential Precision for First Quarter 1982.

1st Value (μg/L)	2nd Value (μg/L)	% Difference
56	55	1.8
43	48	11.0
94	103	9.1
31	47	41.0
70	68	2.9
69	60	14.0
145	139	4.2
43	40	7.2
119	115	3.4
419	423	1.0
614	609	0.8
362	366	1.1
991	978	1.3
268	275	2.6
508	516	1.6
1903	1430	28.4
87	88	1.1
267	287	7.2
608	572	6.1
393	384	2.3
64	67	4.6
380	385	1.3
221	217	1.8
762	747	2.0
915	932	1.8
599	608	1.5
263	264	.4
537	474	12.5
659	663	0.6
1646	1491	9.9
594	560	5.9
725	725	0.0

$n = 42$

$\bar{x} = 6.0$
$s = 8.6$

Table 14. Trihalomethane Formation Potention Precision.

Quarter-Year	1st Value (μg/L)	2nd Value (μg/L)	% Difference
2-1982	164	162	1.2
	110	114	3.6
	80	80	0.0
	21	21	0.0
	1333	1356	1.7
	14	14	0.0
	342	327	4.5
	493	472	4.4
	516	504	2.4
	429	401	6.7
	384	369	4.0
	519	519	0.0
	406	413	1.7
	1130	1091	3.5
	299	284	5.1
	1316	1314	0.2
	624	594	4.9
	717	804	11.4
			n = 18 $\bar{x}$ = 3.1 s = 3.0
3-1982	3595	3595	0.0
	1396	1449	3.7
	1057	1111	5.0
	1632	1610	1.4
	5165	5165	0.0
	625	625	0.0
	594	537	10.1
	2965	3115	4.9
	2134	1799	17.0
	1156	1077	7.1
	1212	1121	7.8
			n = 11 $\bar{x}$ = 5.2 s = 5.2

(continued)

Table 14. (continued)

Quarter-Year	1st Value (µg/L)	2nd Value (µg/L)	% Difference	
4-1982	5425	6490	17.9	
	893	719	21.6	
	1178	1054	11.1	
	979	982	0.3	
	5176	4108	23.0	
	1227	1437	15.8	
	1511	1313	14.0	
	1543	1382	11.0	
	1276	1190	7.0	
	311	412	27.9	
	540	474	14.1	
	409	363	11.9	
	427	396	7.5	
	290	278	4.2	
				n = 14
				$\bar{x}$ = 13.4
				s = 7.6
1-1983	267	216	21.1	
	103	96	7.0	
	194	195	0.5	
	330	334	1.2	
	561	498	11.9	
	607	519	15.6	
	375	295	23.9	
	532	498	6.6	
	199	175	12.8	
	418	347	18.6	
	599	573	4.4	
				n = 11
				$\bar{x}$ = 11.2
				s = 8.0
2-1983	578	610	5.4	
	529	523	1.1	
	320	315	1.6	
	348	363	4.2	
	368	368	0.0	
	361	465	25.2	
	507	463	9.1	
				n = 7
				$\bar{x}$ = 6.7
				s = 8.7

high rate at which precision limits were exceeded during and following the fourth quarter of 1982 is probably associated with new personnel taking over analytical duties. Overall precision was 7.0% with the standard deviation 7.7%. The limit of 20% was exceeded ten times out of 135 duplicate pairs or 7% of the time. Figure 15 shows the distribution of differences for these data.

Accuracy refers to the degree of difference between observed and known or actual values. Accuracy for THM measurements was determined in two manners. The first was an internal method in which spiked samples were analyzed and the percentage of recovery determined. The second method was by participation in EPA Performance Evaluations. The results from these programs will be presented later in a separate section.

During the initial phases of the project, a quality control data collection program was initiated. The results of these analyses are given in Table 15. Four chemical species were analyzed: chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), dibromochloromethane ($CHClBr_2$), and bromoform ($CHBr_3$).

The average recovery for thirteen samples containing chloroform was 102% with a range of 87-135% recovery. The sample with 135% recovery had very low chloroform concentration so the relatively small error (1.5 μg/L) represented a very large error in recovery. The range of recoveries for chloroform was the highest of the four THM species whereas the average percentage of recovery was the closest to 100%.

Dichlorobromomethane recoveries varied from 89% to 116% with an average of 109%. Average percentage of recovery was the highest for this species. Dibromochloromethane had a range of recoveries from 91% to 119% and average recovery of 107%. Bromoform varied from 94% to 122% recovery and had an average recovery of 108%.

Of the 47 recoveries, two or 4.3% were outside of the range 80-120% recovery. Only 17 samples, 36%, had recoveries of less than 100%. This fact together with the fact that all of the average recoveries were greater than 100% indicate that the analyses might be positively biased.

A second data set was compiled in January 1982, to confirm the results of accuracy determinations as shown in Table 16. Of the 38 values, only one value (2.8%) was more than 20% removed from the time or expected value. In the second set of samples, the majority of data appeared biased in the

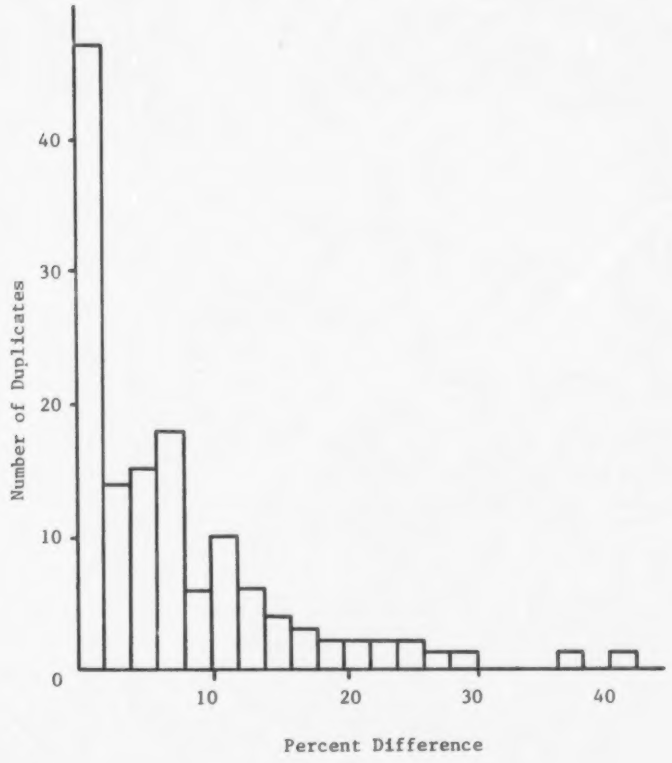


Fig. 15. Distribution of trihalomethane formation potential precision.

Table 15. Trihalomethane Accuracy for 1981.

	$CHCl_3$			$CHCL\ Br_2$			$CHClBr_2$			$CHBr_3$	
Expected (µg/L)	Found (µg/L)	Percent Recovery	Expected (µg/L)	Found (µg/L)	Percent Recovery	Expected (µg/L)	Found (µg/L)	Percent Recovery	Expected (µg/L)	Found (µg/L)	Percent Recovery
10.2	10.0	98	22.8	26	114	11.8	14	119	32.9	36	109
76.6	78	102	91.2	93	102	71.1	79	111	98.7	104	105
100.0	104	104	100	110	110	100	106	106	100	102	102
40.0	41.0	103	40.0	46	115	40	44	110			
114.0	119	104	115	129	112	113	116	103			
124.0	122	98	119	121	102	105	113	108			
40.0	42	105	40	45	113	40	44	110			
223	214	96	137	122	89	109	117	107			
30.0	27.5	92	7.48	8.6	115	7.55	8.4	111	1.39	1.3	94
4.29	5.8	135	1.78	1.9	107	2.52	2.3	91	4.85	5.9	122
14.9	13.0	87	94.4	108	114	11.3	13	115	24.5	29	118
44.7	46	103	61.4	71	116	18.9	19	101	84.8	97	114
125	129	103	115	125	109	110	116	105	100	102	102
		n = 13			n = 13			n = 13			n = 8
		$\bar{x}$ = 102			$\bar{x}$ = 109			$\bar{x}$ = 107			$\bar{x}$ = 108
		s = 11			s = 7.6			s = 6.9			s = 9.3

Table 16. Trihalomethane Accuracy for 1982.

	$CHCl_3$			$CHCL\ Br_2$			$CHClBr_2$			$CHBr_3$	
Expected (µg/L)	Found (µg/L)	Percent Recovery	Expected (µg/L)	Found (µg/L)	Percent Recovery	Expected (µg/L)	Found (µg/L)	Percent Recovery	Expected (µg/L)	Found (µg/L)	Percent Recovery
50	46	92	50	48	96	50	53	106	50	45	90
40	37	93	40	38	95	40	48	120	40	38	95
20	18	90	20	21	105	20	24	120	20	14	70
50	46	92	50	46	92	50	53	106	50	49	98
100	93	93	100	94	94	100	96	96	100	86	86
50	41	82	50	44	88	50	44	88	50	50	100
100	87	87	100	90	90	100	85	85	100	96	96
50	40	80	50	55	110	50	51	102	50	51	102
125	29	103	115	125	109	110	115	105	100	103	103
		n = 9			n = 9			n = 9			n = 9
		$\bar{x}$ = 90			$\bar{x}$ = 98			$\bar{x}$ = 103			$\bar{x}$ = 93
		s = 6.8			s = 8.2			s = 12.2			s = 10.3

negative direction. The exact cause of data biasing was not discovered, however the magnitude of the error was within the 20 percent acceptance region.

Recovery data for spiked samples run since January 1982 are given in Table 17. These data, expressed as percentage of recovery for all THM, (i.e., the sum of the four THM concentrations) had an average recovery of 98% with a standard deviation of 3.4%. The range was 92% - 102%.

The recovery data for THM's have been summarized in Figures 16, 17, 18, 19 and 20. These figures show the standard deviation of the average percentage of recovery of spikes for each THM species and total. They range between 109% and 97% recovery. There was little difference among the percentage of recovery for any of the species or total. The range of this standard deviation was approximately 20% which is expected for THM analysis.

6.4.2 TOC

Analytical precision for TOC determinations was determined by performing duplicate TOC analyses. In the initial phases of the project, 28 sets of duplicate analyses were performed and the percentage of difference determined. These data are given in Table 18 for 1981. The average difference between duplicate analyses was 2.0% with a range of 0 to 9.6% and a standard deviation of 2.4%. Of the 28 duplicate sample pairs, in only three pairs or about 10% did the range exceed 5% of the mean.

In January 1982 a second set of duplicate samples was analyzed containing 18 pairs of duplicate samples. These data are given in Table 19 for 1982. Of the 18 pairs, in only two pairs or about 11% did the range exceed 5% of the mean. The average difference was 2.1% and the standard deviation was 2.1%. Overall precision is shown in Figure 21. Of the 46 duplicate analyses, in only five pairs, or about 10% of the total, did the range exceed 5% of the average.

During the initial stages of the project, two quality control samples were received from EPA for analysis. While not a part of a Performance Evaluation, the samples were useful in determining the accuracy of the TOC analysis. The results may be seen in Table 20. As shown in the table, the laboratory results were very good with 0% difference for the 6.1 mg/L standard and errors of only 0.4% and 1.0% for the higher standard of 91.8 mg/L.

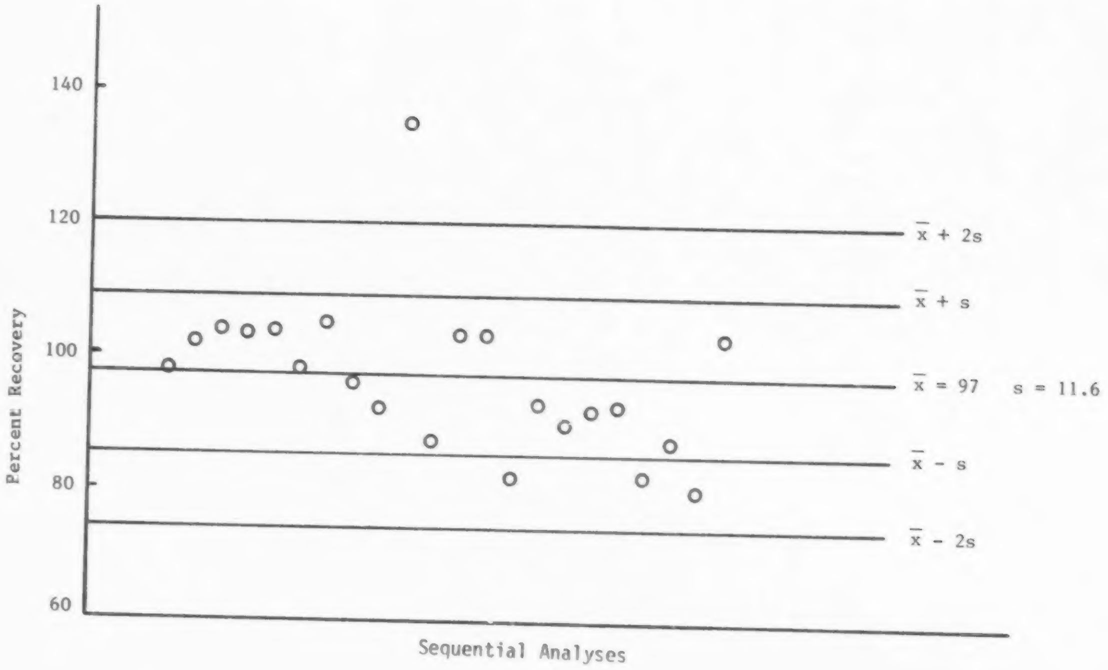


Fig. 16. Chloroform recovery.

Table 17. Trihalomethane Accuracy for Total of All THM Species.

DATE	SAMPLE	SPIKE	% RECOVERY
04-14-82	FW2A	50 (μg/L)	101%
04-14-82	FW3A	100 (μg/L)	96%
04-19-82	FWIN	50 (μg/L)	102%
04-23-82	FW2b	50 (μg/L)	96%
06-03-82	FW4A	50 (μg/L)	92%
06-17-82	FW3C	50 (μg/L)	102%
07-01-82	RW2	100 (μg/L)	96%
07-15-82	FW3A	50 (μg/L)	102%
03-14-83	FW2d	20 (μg/L)	101%
04-08-83	FW2b	50 (μg/L)	96%

$N = 10$
$\bar{x} = 98$
$s = 3.4$

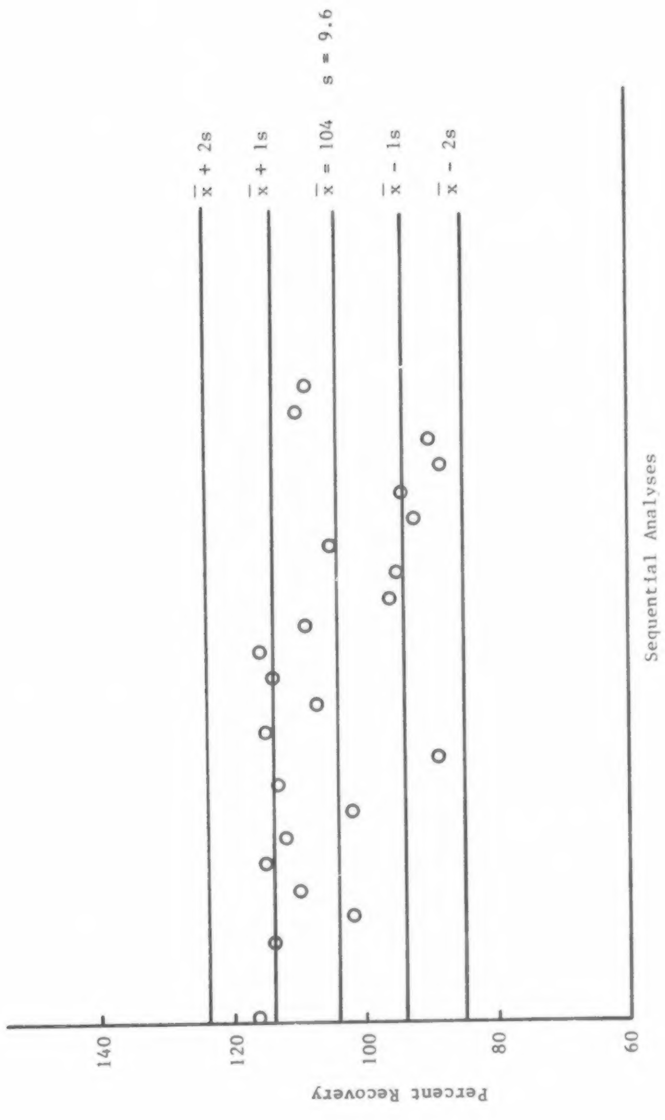


Fig. 17. Bromodichloromethane recovery.

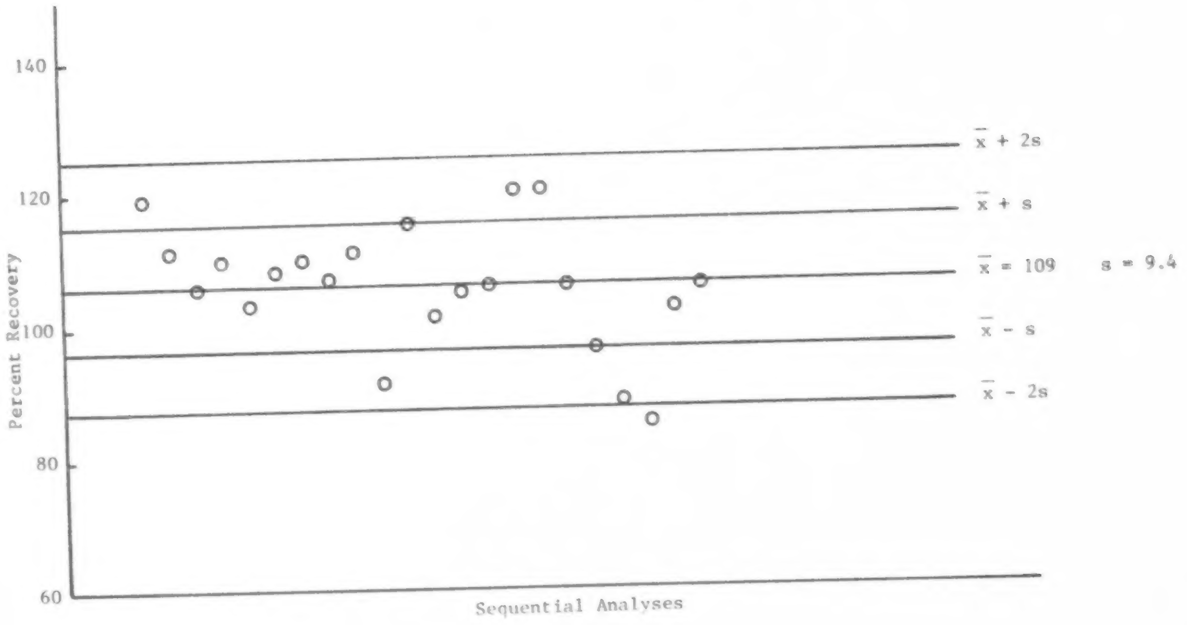


Fig. 18. Dibromochloromethane recovery.

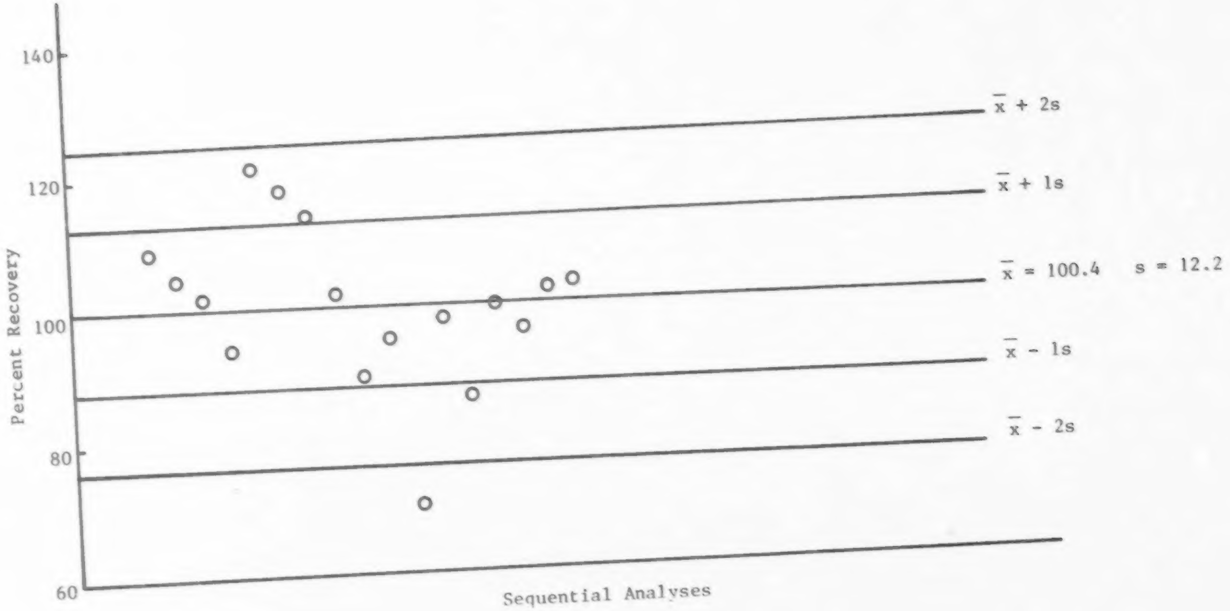


Fig. 19. Bromoform recovery.

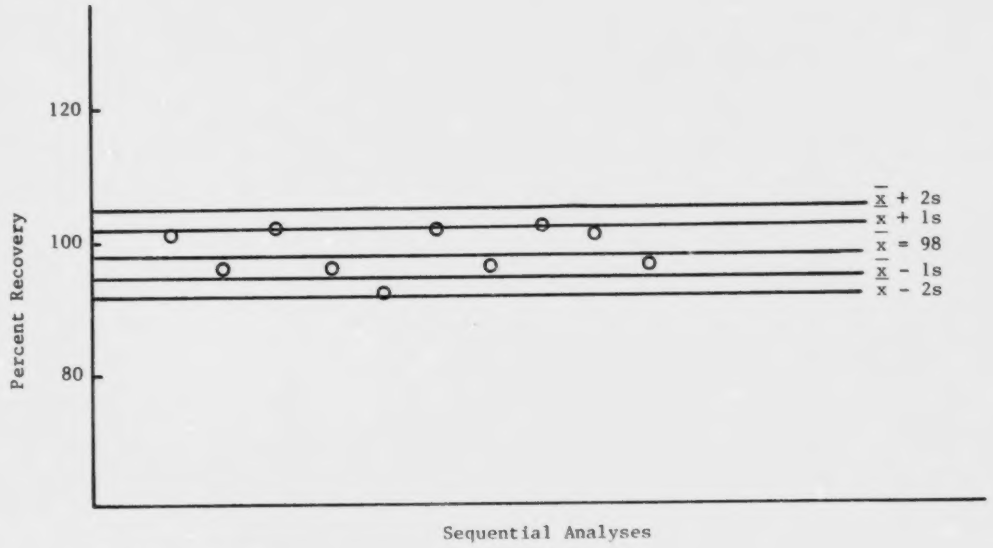


Fig. 20. Total trihalomethane recovery.

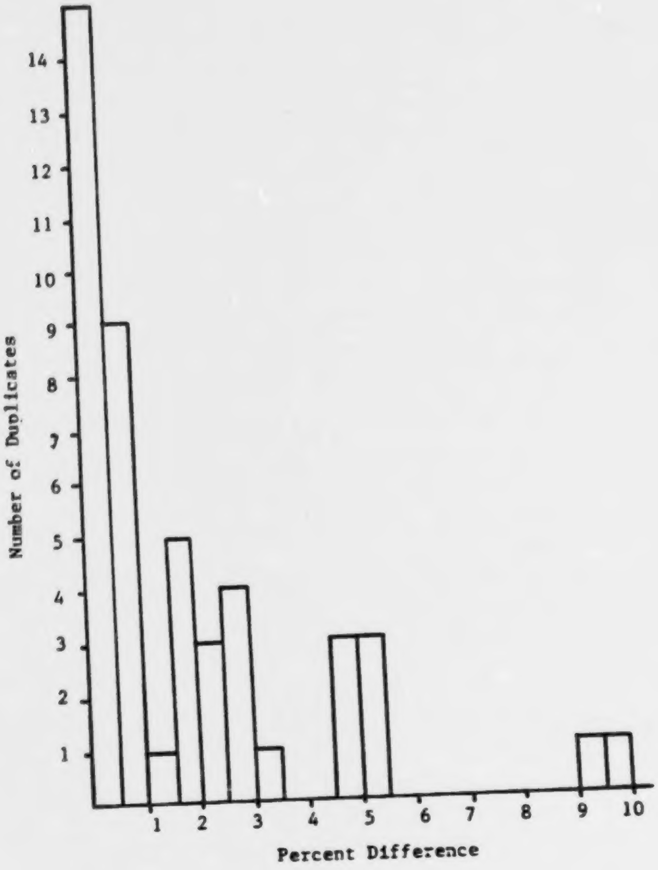


Fig. 21. TOC precision.

Table 18. Total Organic Carbon Precision for 1981.

1st Value (mg/L)	2nd Value (mg/L)	% Difference
719	722	0.4
560	556	0.7
553	544	1.6
547	548	0.2
13.9	14.6	4.9
23.6	26.0	9.7
18.4	18.5	.5
22.1	20.2	9.0
17.4	17.6	1.1
18.0	18.3	1.7
15.7	15.3	2.6
16.0	16.2	1.2
18.0	17.7	1.7
15.8	16.0	1.3
16.7	16.6	0.6
16.1	16.5	2.5
16.3	16.7	2.4
13.3	13.6	2.2
13.4	13.9	3.7
13.4	13.3	0.7
9.3	9.4	1.1
10.2	10.2	0
9.8	9.6	2.1
10.4	10.1	2.9
9.6	9.6	0
10.8	10.9	0.9
9.4	9.4	0
10.1	10.1	0

$n = 28$
$\bar{x} = 2.0$
$s = 2.4$

Table 19. Total Organic Carbon Precision 1982.

1st Value (mg/L)	2nd Value (mg/L)	% Difference
16.0	15.9	0.6
15.9	15.0	5.8
15.8	15.8	0.0
15.7	15.5	1.3
15.0	14.9	0.7
15.3	15.2	0.7
15.3	15.2	0.7
14.9	15.0	0.7
20.9	19.9	4.9
28.9	27.5	5.0
541.0	513.0	5.3
25.6	25.5	0.4
14.6	23.9	2.9
15.4	15.0	2.6
16.4	17.2	4.8
25.2	25.0	0.8
15.5	15.6	0.6
24.5	24.6	0.4

$\underline{n} = 18$
$\bar{x} = 2.1$
$s = 2.1$

Table 20. Total Organic Carbon Accuracy.

True Value.	Analyst 1		Analyst 2	
True Value (mg/L)	Found (mg/L)	% Recovery	Found (mg/L)	% Recovery
6.1	6.1	100	6.1	100
91.8	90.8	99	91.4	100

6.4.3 Hardness

During the initial stages of the project, accuracy was determined for the analysis of total hardness. Spiked samples were analyzed and 70 recoveries were determined. An average recovery of 103.5% was found for the nine samples. The range was from 100 to 109% recovery. Three Ca-Hardness samples were analyzed with all three samples exhibiting 100% recovery.

6.5 EPA Quality Control Program

The quality control program included participation in a regularly scheduled EPA Laboratory Performance Evaluation. This laboratory has participated in four studies (WS007, WS008, WS010, and WS012). In these studies, all participating laboratories analyze identical samples, and the acceptable range is determined from the results. Table 21 gives a summary of the results for this laboratory.

6.5.1 Chloroform ($CHCl_3$)

Of the six samples analyzed, two samples were found to be outside of the acceptable range, as established by the study participants. In both cases, the samples had low concentrations (20 μg/L or less) and the error was less than 5 μg/L. In the remaining samples, the error was generally less than 2 μg/L.

6.5.2 Bromoform ($CHBr_3$)

All six samples in the three studies were found to be in compliance. While the absolute difference between the reported value and the true value tended to be larger than found for chloroform, all samples were comfortably inside the acceptable range.

6.5.3 Bromodichloromethane ($CHCl_2Br$)

All six samples were found to be within the acceptable range. In most of the cases the observed difference was 4 μm/L or less. The other analyses were also well within the acceptable limit.

6.5.4 Dibromochloromethane ($CHClBr_2$)

All samples were found to be within the acceptable range. This chemical species tended to have the largest differences between the observed and true values. However, only one sample was close to the limit.

6.5.5 Trihalomethanes

All samples were found to be in compliance by a comfortable margin.

Table 21. Performance Evaluation Summary.

		WS-7		WS-8		WS-10		WS-12	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
$\mathrm{ChCl_3}$									
Reported	µg/L	13	46	78	10	63.4	15.9*	4*	41
True	µg/L	14.9	44.7	76.6	10.2	61.3	20.4	5.93	35.6
Accepted Range	µg/L	12-18	36-54	61-92	8.2-12.2	49-74	16-24	4.74-7.12	28.5-42.7
$\mathrm{CHBr_3}$									
Reported	µg/L	29	71	104	36	83.5	18.1	30	71
True	µg/L	24.5	61.4	98.7	32.9	82.3	21.9	30.5	67.7
Accepted Range	µg/L	20-29	49-74	79-120	26-39	66-99	18-26	24.4-36.6	54.2-81.2
$\mathrm{CHCl_2Br}$									
Reported	µg/L	108	19	93	26	81.2	27.7	16	45
True	µg/L	94.4	18.9	91.2	22.8	73.0	27.4	14.1	42.3
Accepted Range	µg/L	76-110	15-23	73-110	18-27	58-88	22-33	22.3-33.5	44.6-67.0
$\mathrm{CHClBr_2}$									
Reported	µg/L	13	97	79	14	57.1	20.4	31	57
True	µg/L	11.3	84.8	71.1	11.8	53.3	23.7	27.9	55.8
Accepted Range	µg/L	9.0-14	68-100	57-85	9.4-14	43-64	19-28	22.3-33.5	44.6-67.0
Total THM									
Reported	µg/L	163	233	354	86	285	82	81	214
True	µg/L	145.1	209.8	337.6	77.7	269.9	93.4	78.4	201.4
Accepted Range	µg/L	120-170	170-250	270-410	62-93	220-320	75-110	62.7-94.1	161-242
Residual Free Chlorine									
Reported	mg/L	0.7	1.7	0.93	1.35	0.73	1.60	.25	.91
True	mg/L	0.5	1.29	0.80	1.10	0.70	1.51	.325	1.08
Accepted Range	mg/L	.23-.85	0.80-1.8	.37-1.2	.63-1.6	.42-.99	1.2-1.8	0.659-.565	.595-1.41
Turbidity									
Reported	NTU	5.3*	0.9	1.31	5.74	1.24	4.95	5.8	0.4
True	NTU	3.5	0.6	1.75	6.0	1.35	5.5	5.9	0.42
Accepted Range	NTU	2.9-4.7	.34-1.1	1.3-2.1	5.2-6.8	.95-1.7	4.6-6.4	5.2-6.62	.184-.655

*Not Acceptable

6.5.6 Residual Free Chlorine

All six samples were found to be in compliance with the absolute difference being generally less than 0.2 mg/L. In particular the latest analyses (WS010) were very close with differences of less than 0.1 mg/L.

6.5.7 Turbidity

Of the six samples only one sample (Sample #1, WS007) was found to be out of the acceptable range. Following an internal review the potentiometer on the nephelometer was replaced and new standards obtained. Following these steps the analysis of turbidity improved so that the absolute difference between the reported value and true value was generally less than 0.5 NTU.

CHAPTER 7

RESULTS AND DISCUSSION

7.0 Introduction

The project was organized so that the subtasks requiring only laboratory and desk top work were done at the University of Central Florida. The water used for project experimentation at UCF was taken weekly from the Melbourne Water Treatment Plant and transported to and stored in the environmental engineering laboratories at UCF. The quality of this raw water at the beginning and end of a week's storage is presented in Table 22. These data indicate that during the first portion of the project there was no predictable variation in any water quality parameter. There were occasions when the SPC increased and the TOC concentration decreased which would indicate biological consumption of TOC, however, no consistent correlations were observed. The changes in these parameters were generally less than 5% during one week's storage and do not appear to significantly affect the project results.

7.1 Jar Test

The basic purpose of the Jar Test Subtask was to optimize the coagulation process for the removal of THM precursors. In this phase there was no InstTHM, so that TermTHM equaled to THMFP. This was accomplished by determining the optimum coagulation pH, magnesium dose, rapid mixing times, slow mixing times and polymer dose in the coagulation process for maximum reduction of THMFP in the coagulated, settled and filtered water. The experiments were conducted in the UCF environmental engineering laboratories.

7.1.1 Coagulation

The $Mg(HCO_3)_2$ recycled coagulant was prepared by two different methods because of differences in plant operation. The first method was in-plant preparation. The normal plant method was to supplement the magnesium sludge from the clarifier with a magnesium rich saline well water before recovery by carbonation so that additional magnesium would be available after recovery. This method was later shown to be detrimental to final water quality. Since

Table 22. Lake Washington Water Quality Variation Due to Storage

BATCH	VI		VII		VIII		IX	
Date:	12/01	12/07	12/07	12/14	12/14	1/06	1/06	1/14
Sample In/Out:	In	Out	In	Out	In	Out	In	Out
pH	7.15	7.7	7.6	7.1	7.6	-	7.9	7.5
TOC mg/l	17.6	11.3	20.5	-	-	-	19.7	21.2
Color cpu	59	57	55	-	-	-	55	50
Alkalinity mg/l $CaCO_3$	-	-	62	-	-	-	-	56
Ca mg/l $CaCO_3$	-	-	108	-	120	-	124	117
Mg mg/l $CaCO_3$	-	-	68	-	69	-	81	72
THMFP µg/l $CHCl_3$	-	-	1380	-	-	-	1081	975
SPC #/100 ml x 10^5	2.02	TNTC	2.36	7.30	2.90	-	4.51	3.40

(continued)

Table 22. (continued)

BATCH	VI		VII		VIII		IX	
Date:	12/01	12/07	12/07	12/14	12/14	1/06	1/06	1/14
Sample In/Out:	In	Out	In	Out	In	Out	In	Out
BATCH	X		XI		XII		XIII	
Date:	1/14	1/21	1/21	1/28	1/28	2/04	2/04	2/11
Sample In/Out:	In	Out	In	Out	In	Out	In	Out
pH	7.7	7.6	7.6	7.7	7.6	7.8	7.8	7.6
TOC mg/l	20.9	18.1	21.9	19.3	17.3	18.9	19.2	18.6
Color cpu	60	55	65	65	48	50	50	50
Alkalinity mg/l $CaCO_3$	83	76	74	72	76	68	64	75
Ca mg/l $CaCO_3$	140	131	136	141	141	105	102	
Mg mg/l $CaCO_3$	83	63	66	110	95	66	60	
THMFP µg/l $CHCl_3$	1817	-	-	855	908	835	875	
SPC #/100 ml x 10^5	17.80	-	-	6.40	7.40	1.23	0.65	

(continued)

Table 22. (continued)

BATCH	XIV		XV		XVI		XVII	
Date:	2/25	3/04	3/04	2/25	2/25	3/04	3/04	3/11
Sample In/Out:	In	Out	In	Out	In	Out	In	Out
pH	7.9	7.7	8.0	8.0	7.7	7.8	8.0	7.0
TOC mg/l	18.9	17.0	19.2	17.7	18.3	18.3	19.4	18.6
Color cpu	55	55	50	50	55	55	55	55
Alkalinity mg/l $CaCO_3$	76	65	82	80	86	89	75	91
Ca mg/l $CaCO_3$	146	141	157	152	171	158	160	156
Mg mg/l $CaCO_3$	82	82	85	100	108	76	67	82
THMFP µg/l $CHCl_3$	667	831	831	794	968	1203	1084	1327
SPC #/100 ml x 10^5	1.17	15.5	48.0	84.0	9.2	5.5	2.9	15.5

(continued)

Table 22. (continued)

BATCH	XVIII		XIX		XX		XXI	
Date:	3/11	3/18	3/18	3/24	3/24	3/31	3/31	4/07
Sample In/Out:	In	Out	In	Out	In	Out	In	Out
pH	7.4	7.7	8.0	8.0	8.0	7.9	8.0	7.7
TOC mg/l	21.5	20.0	20.6	20.6	21.1	19.0	20.6	19.7
Color cpu	75	65	60	60	65	65	65	65
Alkalinity mg/l $CaCO_3$	93	87	95	95	91	93	96	95
Ca mg/l $CaCO_3$	160	164	166	166	180	168	170	160
Mg mg/l $CaCO_3$	72	90	103	62	78	79	70	56
THMFP µg/l $CHCl_3$	1106	1207	1121	900	954	1165	1373	1240
SPC #/100 ml x 10^5	15.0	80.0	86.0		86.0	26.0	69.0	97.0

(continued)

Table 22. (continued)

BATCH	XXII		XIII		XXIV		XXV	
Date:	4/07	4/14	4/14	4/21	4/21	4/29	4/29	5/06
Sample In/Out:	In	Out	In	Out	In	Out	In	Out
pH	7.7	7.7	7.9	7.5	7.5	7.7	8.0	8.0
TOC mg/l	20.9	21.9	22.7	20.8	21.4	23.6	32.8	21.1
Color cpu	70	65	65	65	65	65	65	65
Alkalinity mg/l $CaCO_3$	93	100	96	100	100	104	106	96
Ca mg/l $CaCO_3$	170	165	170	167	176	175	180	174
Mg mg/l $CaCO_3$	70	60	80	73	57	79	72	97
THMFP µg/l $CHCl_3$	1107	1474	1580	1186	1075	1376	1329	1208
SPC #/100 ml x 10^5	18.3	23.4	4.0	17.2	22.0	2.0	4.5	4.5

(continued)

Table 22. (continued)

BATCH	XXIX		XXXIII		XXXVIII	
Date:	6/03	6/10	6/30	7/07	8/04	8/11
Sample In/Out:	In	Out	In	Out	In	Out
pH	7.9	7.2	7.9	7.8	7.6	7.4
TOC mg/l	22.4	20.9	24.62	23.63	29.09	22.72
Color cpu	65	60	55	55	60	60
Alkalinity mg/l $CaCO_3$	116	116	105	102	95	97
Ca mg/l $CaCO_3$	200	200	198	202	212	214
Mg mg/l $CaCO_3$	81	81	72	74	90	93
THMFP µg/l $CHCl_3$	1191	1797	1280	1771	1242	1699
SPC #/100 ml x 10^5	---	15.9	6.2	8.3	3.5	3.8

the plant ceased to prepare any recycle $Mg(HCO_3)_2$, a second method was developed where clarifier sludge was brought directly to UCF laboratories and carbonated forming $Mg(HCO_3)_2$. Both sources of recycle $Mg(HCO_3)_2$ were used in jar testing with differing results. Figures 22 through 27 are isopleths that indicate percentage removal for either color, TOC or THMFP as a function of recycled $Mg(HCO_3)_2$ coagulant dose and coagulation pH. Since Mg^{++} ions are available in the raw water at Melbourne, the total Mg^{++} ions available for coagulation would be the Mg^{++} ions dosed plus the raw water Mg^{++} ions.

As shown in Figures 22 through 27, removal of THMFP corresponds directly to removal of TOC or color. The maximum reductions of THMFP, TOC and color occurred at the highest coagulation pH (12) and lowest recycled $Mg(HCO_3)_2$ dose (0 mg/L) for samples treated with $Mg(HCO_3)_2$ prepared from the saline well water and clarifier sludge. This is shown in Figures 22, 23 and 24. However, for samples treated either with $Mg(HCO_3)_2$ prepared by only carbonating the clarifier sludge or with $MgSO_4$, the maximum THMFP, TOC and color removal generally occurred at the highest coagulation pH (12) and magnesium dose (40 mg/L as Mg^{++}). This is shown in Figures 25, 26 and 27 and is supported by the data presented in Figure 7 from the plant evaluation study in 1982. The most significant finding of the jar test phase was that conventional recycled $Mg(HCO_3)_2$ prepared only from recarbonation of clarifier sludge and used as a coagulant would improve final water quality, but recycled $Mg(HCO_3)_2$ prepared with saline well water would degrade final water quality. However, conventional recycled $Mg(HCO_3)_2$ would remove as much color, TOC or THMFP during coagulation as would fresh $MgSO_4$.

The effect of varying lime sources is shown in Figures 22, 23 and 24. The maximum color reduction using saline recycled magnesium varies from 78% to 85% of the initial color, as seen in Figures 22, 23 and 24. There was slightly less color removed with commercial lime than with either reagent or recalcined lime, which amounted to approximately 3 cpu's. This was attributed to the higher organic content of commercially mined lime versus reagent or recalcined lime. TOC removal as indicated in Figures 22, 23 and 24 varied from 49% to 38% with commercial lime again achieving less TOC removal (approximately 2 mg/L) than either reagent or recalcined lime. The THMFP reduction as shown in Figures 22, 23 and 24, indicates that commercial lime faired slightly better than recalcined lime with a 41% to 46% THMFP reduction or a

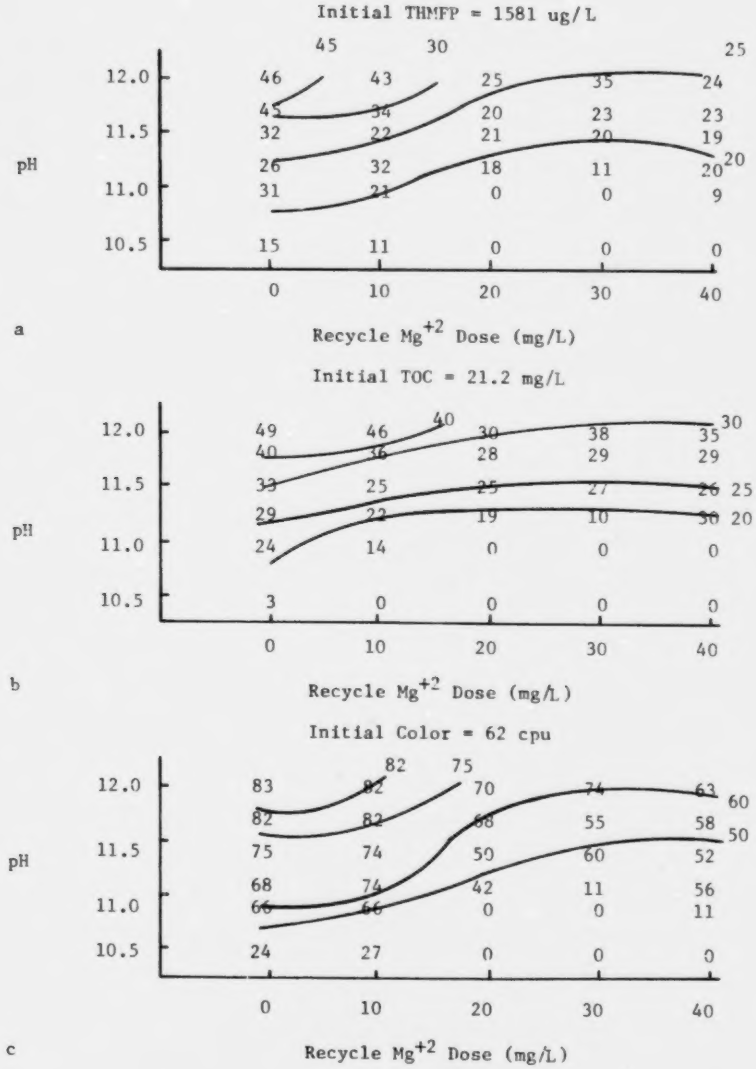


Fig 22. Isopleths for percent removal of (a) THMFP, (b) TOC, and (c) color for a low color, high magnesium Lake Washington water treated by coagulation with recycle magnesium prepared from saline well water and pure reagent lime. Magnesium concentration in the raw water was 15 mg/L as ion.

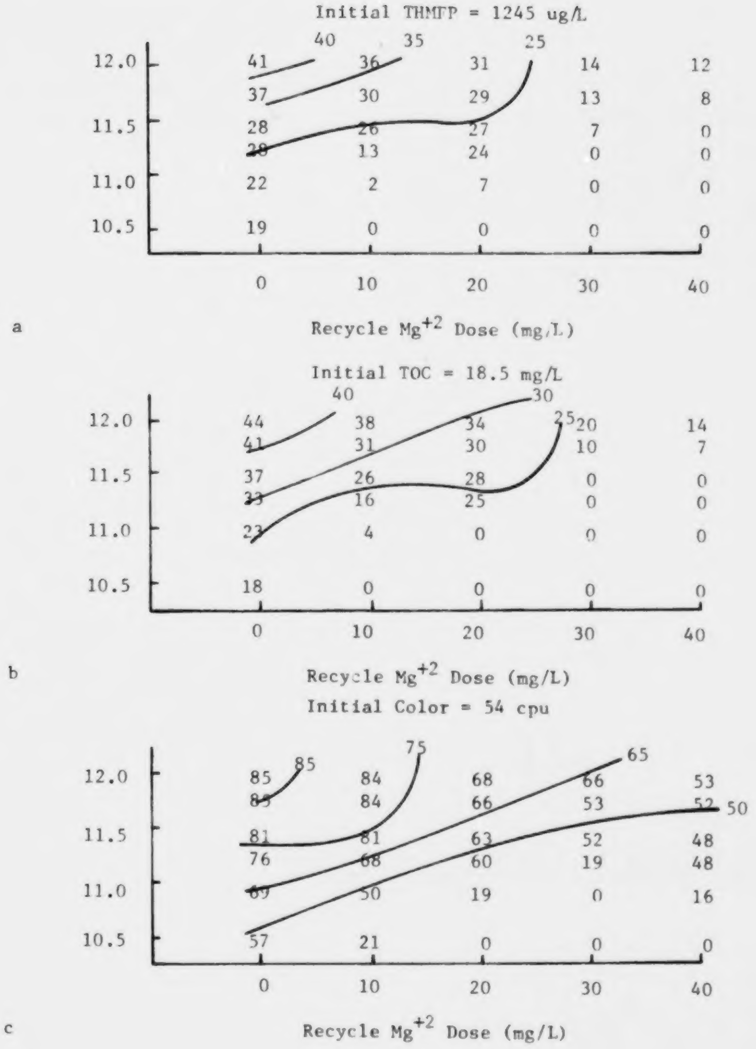
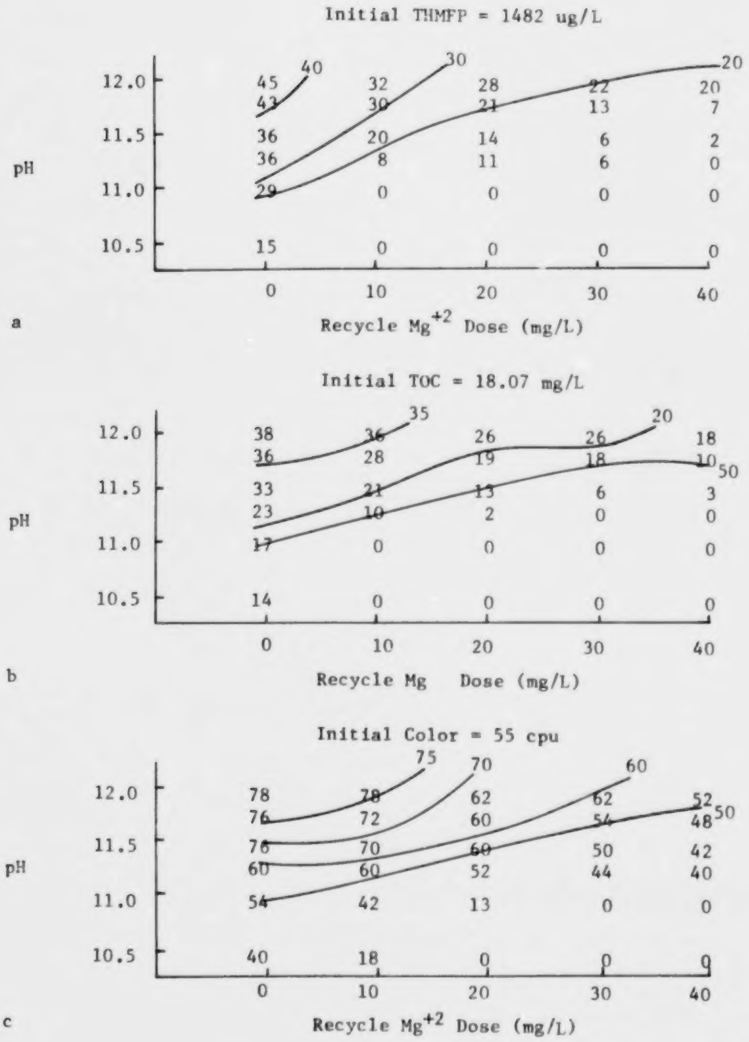


Fig. 23. Isopleths for percent removal of (a) THMFP, (b) TOC, and (c) color for a low color, high magnesium Lake Washington water treated by coagulation with recycle magnesium prepared from saline well water and recalcined lime. Magnesium concentration in the raw water was 20 mg/L as ion.



Initial THMFP = 1482 ug/L

Initial TOC = 18.07 mg/L

Initial Color = 55 cpu

Fig. 24. Isopleths for percent removal of (a) THMFP, (b) TOC, and (c) color for a low color, high magnesium Lake Washington water treated by coagulation with recycle magnesium prepared from saline well water and commercial lime. Magnesium concentration in the raw water was 26 mg/L as ion.

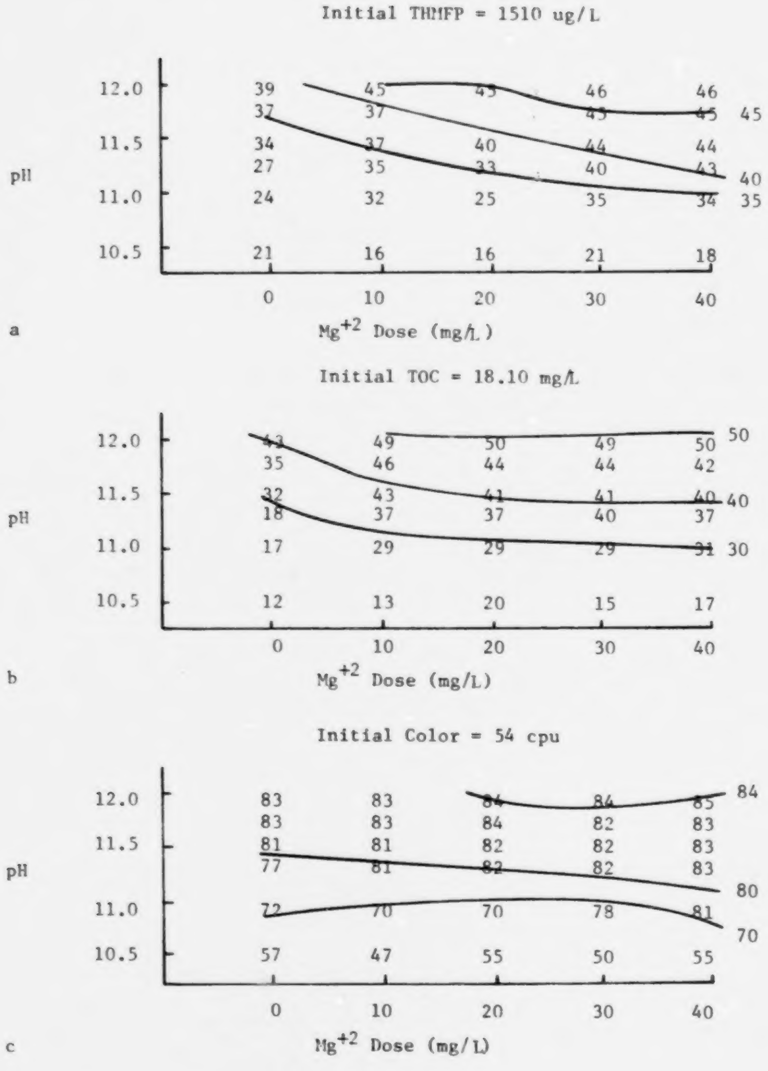


Fig. 25. Isopleths for percent removal of (a) THMFP, (b) TOC, and (c) color for a low color, high magnesium Lake Washington water treated by coagulation with fresh magnesium sulfate and recalcined lime. Magnesium concentration in the raw water was 18 mg/L as ion.

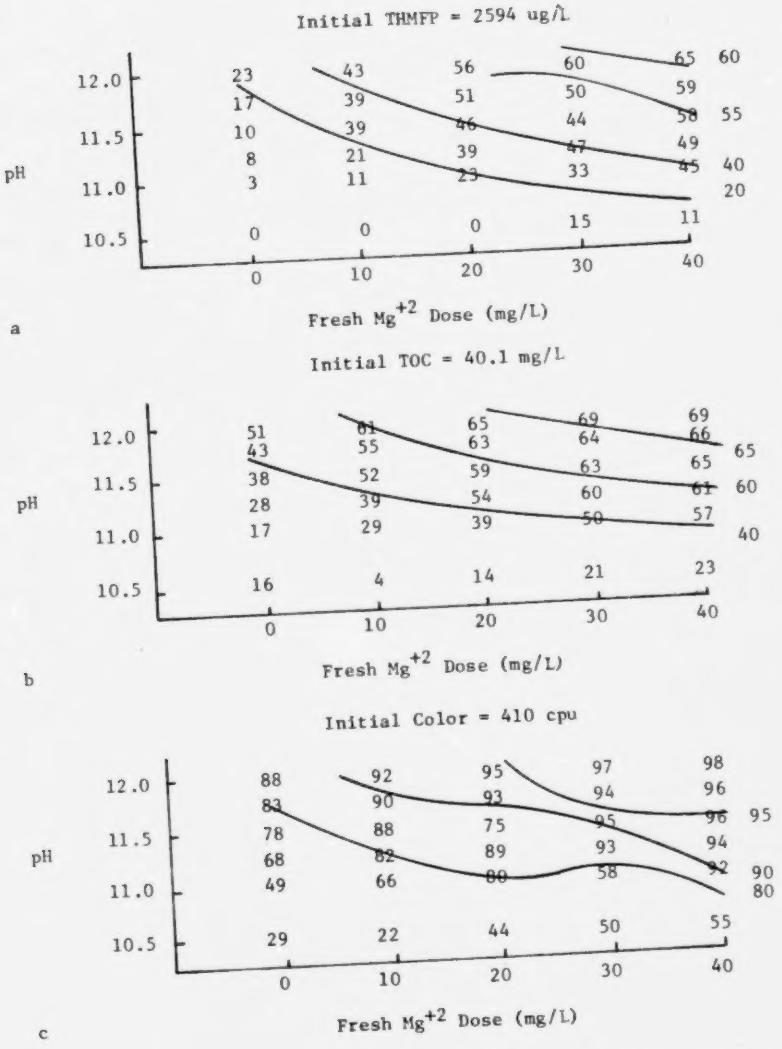


Fig. 26. Isopleths for percent removal of (a) THMFP, (b) TOC, and (c) color for a high color, low magnesium Lake Washington water treated by coagulation with fresh magnesium sulfate and recalcined lime. Magnesium concentration in the raw water was 5 mg/L as ion.

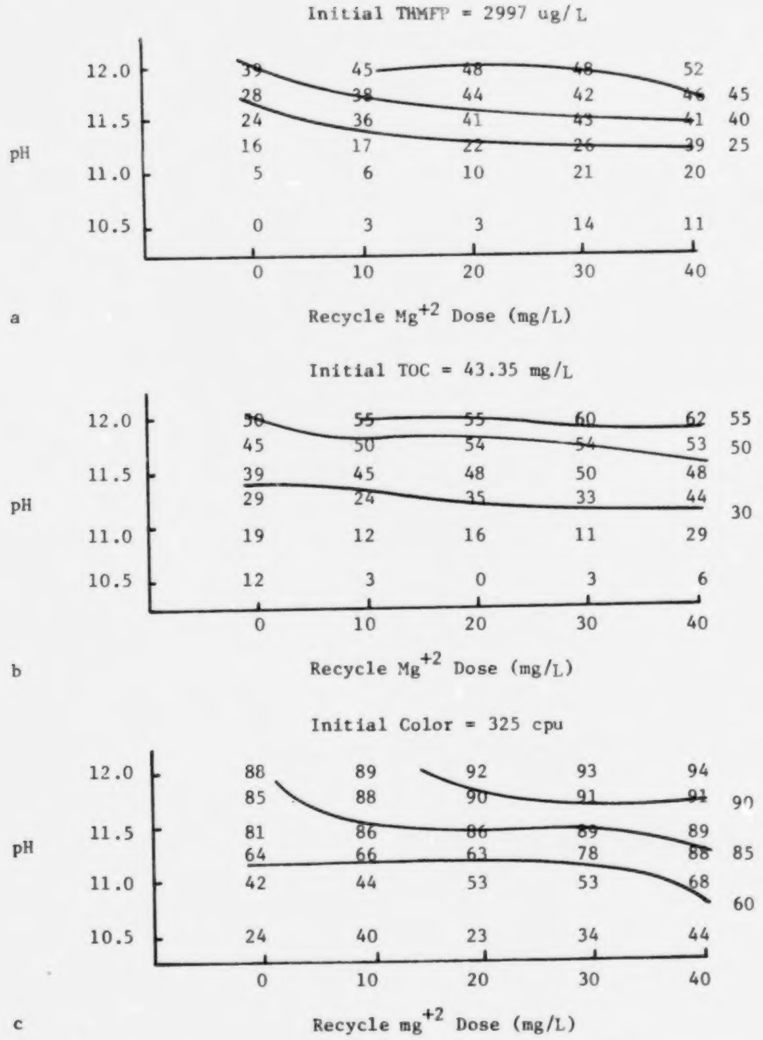


Fig. 27. Isopleths for percent removal of (a) THMPF, (b) TOC, and (c) color for a high color, low magnesium Lake Washington water treated by coagulation with conventional recycle magnesium and recalcined lime. Magnesium concentration in the raw water was 5 mg/L as ion.

difference of approximately 80 μg/L between the top and bottom of the range. These small differences in removal of color, TOC or THMFP indicate that the most economical form of lime (commercial) should be used in the plant.

A chlorine dose of 60 mg/L was necessary in order to achieve a free chlorine residual at the end of the 48-hour THM formation period. This is higher than the chlorine dose used at Melbourne (15-25 mg/L), but was necessary to achieve consistency in THM formation. The lack of $Mg(OH)_2$ precipitation at pH's below 11 results in limited, if any, precursor removal, which in turn requires a large chlorine dose to guarantee a free chlorine residual after a 48-hour formation period. Additionally, the data in Figures 22 to 27 indicate a minimum pH of 11.3 for organic removal.

The average magnesium concentration in the raw water was 20.3 mg/L Mg^{++} which was available during coagulation. Since the optimum pH was 12 and no additional magnesium was added for the saline recycle, virtually all of the magnesium or 0.84 mmol/l of Mg^{++} was removed during coagulation. This resulted in average color, TOC and THMFP reductions of 47 cpu's, 0.70 mmols/L and 0.01 mmols/L, respectively. The ratios of color, TOC and THMFP removed to Mg^{++} removed are 56 cpus/mmol Mg^{++}, 0.83 mmol TOC/mmol Mg^{++} and 9.01 umol THMFP/mmol Mg^{++} for the data given in Figures 22, 23 and 24.

The data in Figures 25 and 26 show that fresh $MgSO_4$ can be used as a coagulant to remove color, TOC or THMFP from a low or high color raw water. The color, TOC and THMFP of the low color water were 54 cpu, 18.10 mg/L and 1510 μg/L. A pH of 11.3 and Mg^{++} dose of 10 mg/L did achieve color, TOC and THMFP removals of 77%, 37% and 35%. If the coagulation pH was increased to 12, 5-10% more of each parameter was removed. An acceptable color of less than 15 cpu could be achieved with a coagulation pH of 11 or more, but a THMFP of 0.10 mg/L could not be obtained by coagulation alone for the low color samples which represent the best quality water experienced at Melbourne. The color, TOC and THMFP of the high color water were 410 cpu, 40.1 mg/L and 2594 μg/L. As in the low color case, maximum removals of color, TOC and THMFP occurred at the highest pH and coagulant dose utilized. However, a pH of 12 and Mg^{++} dose of 30 mg/L, at pH 12, was required to reduce the color to less than 15 cpu. The THM MCL of 0.10 mg/L was never obtained, and 0.91 mg/L was the best achieved. The corresponding TOC was 12.3 mg/L.

The data presented in Figure 27 show that conventionally prepared recycled $Mg(HCO_3)_2$ can be used successfully as a coagulant. The initial color, TOC and THMFP were 325 cpu, 43.35 mg/L and 2997 μg/L. These values were reduced by coagulation at pH 12 and 40 mg/L Mg^{++} by 94%, 62% and 52%, respectively, leaving 20 cpu color, 16.5 mg/L TOC and 1439 μg/L THMFP. Neither the 15 cpu color standard nor the 0.10 mg/L THM MCL was achieved. Although the recycled $Mg(HCO_3)_2$ was a successful coagulant, it was not generally as effective as fresh $MgSO_4$, which typically removed about 5-10% more color, TOC and THMFP at equivalent pH's and doses.

Some analysis was done to determine a guide for coagulant dose during plant operation. Since color removal is the operational parameter at most plants, and color removal responded as did TOC or THMFP, color was selected as a basis for determining coagulant dose. The data in Figures 22 through 27 do not readily yield a color/Mg^{++} ratio during coagulation, but a general observation would be that a color/Mg^{++} ratio of 10 to 5 cpu/mg/L at pH 11.5 would produce satisfactory treatment. Such practice would normally achieve reductions of 80-90% color, 40-50% TOC and 35-45% THMFP removal. These removals may average 5% less than could be achieved with fresh $MgSO_4$ and 10 to 15% less than could be achieved by alum as indicated by the 1982 plant evaluation and Hatcher (1981).

7.1.2 Solubility

Magnesium (saline $Mg(HCO_3)_2$) solubility as a function of pH in Lake Washington raw water using different lime sources is presented in Figure 28. This was done to determine if incomplete magnesium precipitation was the cause of the color addition from the saline $Mg(HCO_3)_2$. There are slightly higher magnesium residuals with commercial lime below pH 11.5 which could be affected by the organic content of the mined commercial lime. However, the magnesium residuals indicate that a pH of 11.5 must be obtained during coagulation to ensure that all the magnesium precipitates from solution, which optimizes treatment. The data in Figure 28 indicate that there is little additional magnesium removed beyond pH 11.5 The additional removal of magnesium, 1-2 mg/L, corresponded to 2-8% color removal, 5-6% TOC removal and 9-14% THMFP removal. This indicates a stoichiometric ratio between magnesium removed and color removed during coagulation. However, 16% of the TOC and 33% of the THMFP removed during coagulation corresponds to the last 5-10% of the

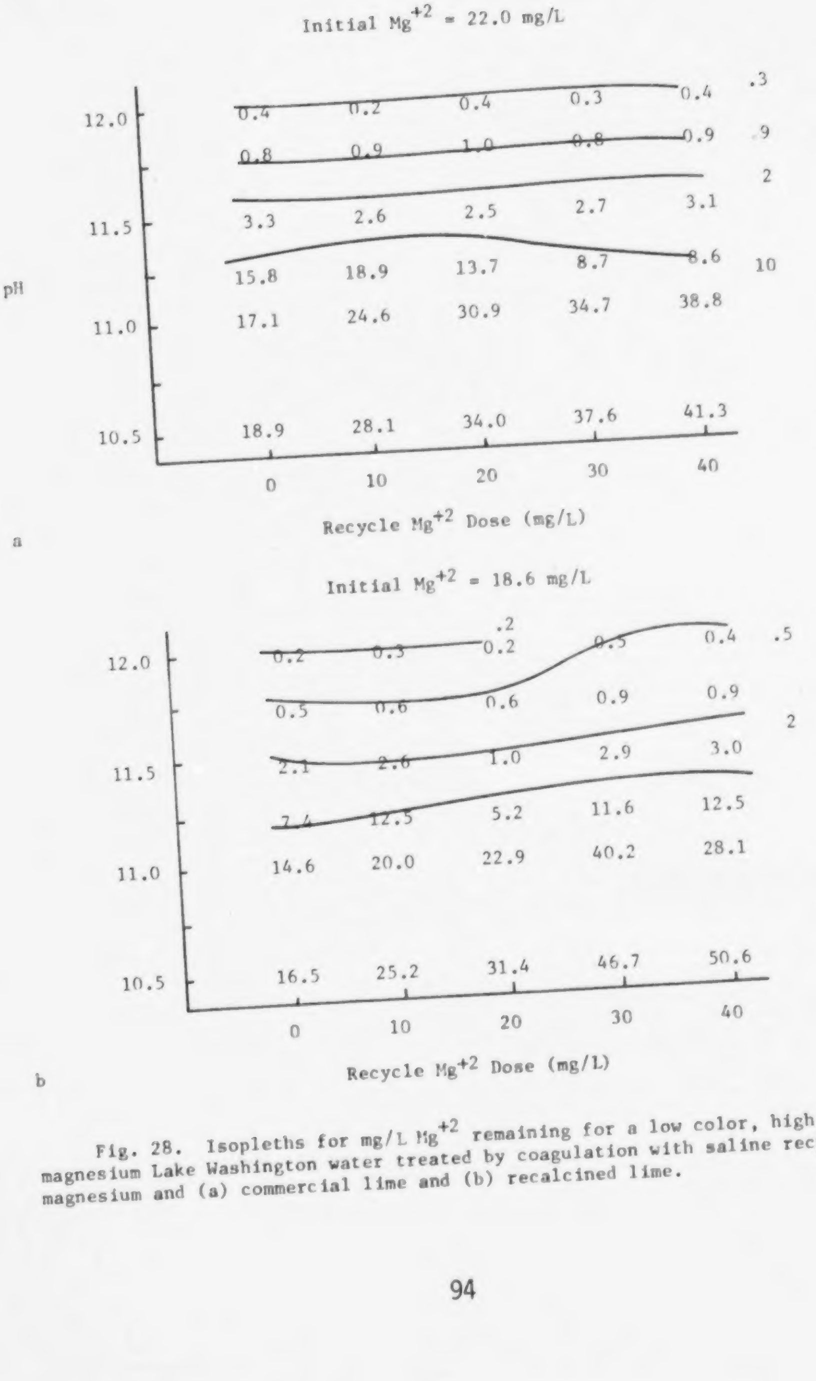


Fig. 28. Isopleths for mg/L Mg^{+2} remaining for a low color, high magnesium Lake Washington water treated by coagulation with saline recycle magnesium and (a) commercial lime and (b) recalcined lime.

magnesium removed, which is why the higher pH's are necessary to optimize coagulation for THMFP, TOC or color removal.

There is no significant difference between the magnesium residuals remaining after coagulation when either recalcined or commercial lime was used to adjust pH. The magnesium residual is reduced to less than 1 mg/L above pH 11.5. The most important finding in Figure 28 is that all of the magnesium comes out of solution as the coagulation pH is increased and recycle dose is increased. That is, if the coagulation pH is 12, the magnesium residual will be 0.5 mg/L Mg^{++} or less, whether zero or 40 mg/L recycle magnesium was used. Therefore, as saline magnesium recycle dose is increased, the increasing color, TOC and THMFP in the finished water cannot be attributed to incomplete magnesium precipitation, but must be due to something in the well water. This could possibly be an adverse effect of the higher ionic strength of the saline well water. This indicates the higher coagulation pH's are more important to treatment than magnesium dose. The data in Figures 22 through 27 for zero Mg^{++} dose shows that approximately 35% more color, 25% more TOC and 20% more THMFP removal can be obtained by raising the pH from 11 to 12 for either the high or low color water. The relationship between coagulation pH and percentage of color removal is linear and is shown in Figure 29. Although the high pH is necessary to make the magnesium precipitate from solution, the low magnesium removal past pH 11.5 accompanied by the continued linear relationship shown in Figure 29, indicates that something else (in addition to magnesium) is responsible for removals at higher pH. Such a phenomenon could help a plant utilizing excess lime softening meet regulation, if the color and THMFP were already close to standard.

The increased hardness of the finished water is shown in Figure 30, which gives calcium residual as a function of pH for three different limes. These data indicate as soon as the carbonate alkalinity is consumed by $CaCO_3$ formation, the calcium residual increases. Some of this calcium could be removed by recarbonation, but the finished hardness at Melbourne will always be 150-200 mg/L $CaCO_3$, as long as a high coagulation pH is utilized to remove maximum organics during coagulation and the raw water quality does not change.

The separate lime sources were investigated because it was suspected that the magnesium solids recalcined in the recalcined lime would provide more

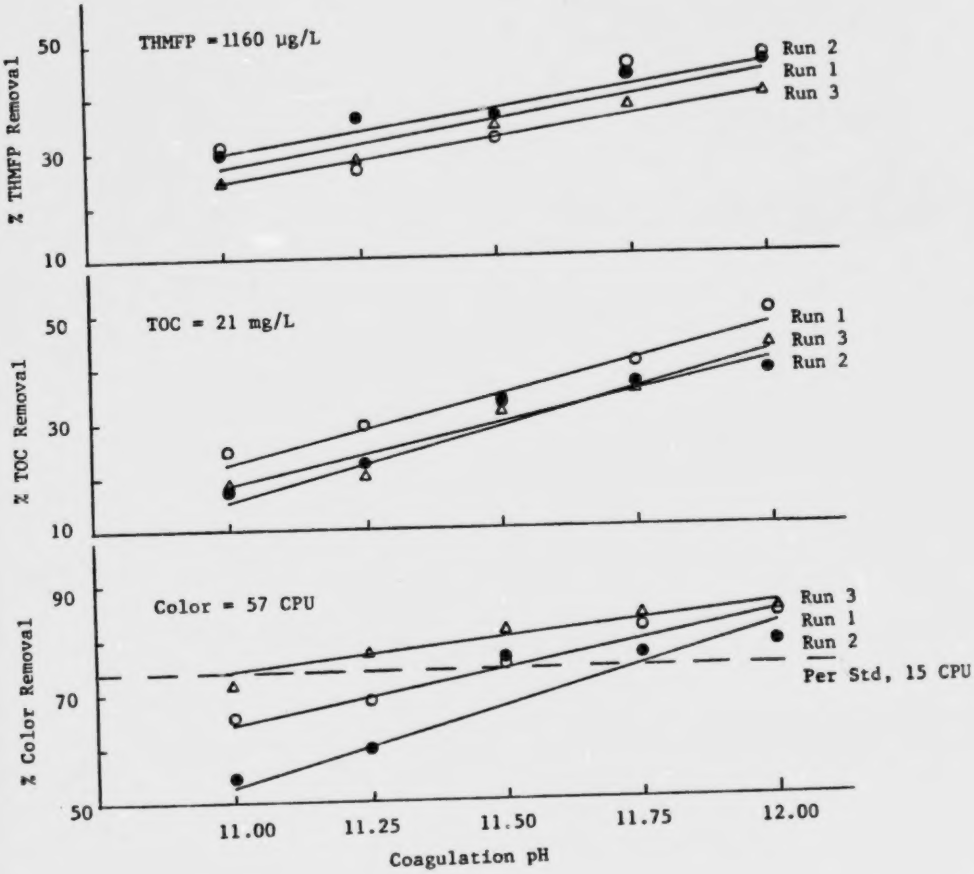


Figure 29 Percent THMFP, percent TOC, and percent color removal as a function of coagulation pH for a low color Lake Washington water with pH 11 taken as baseline.

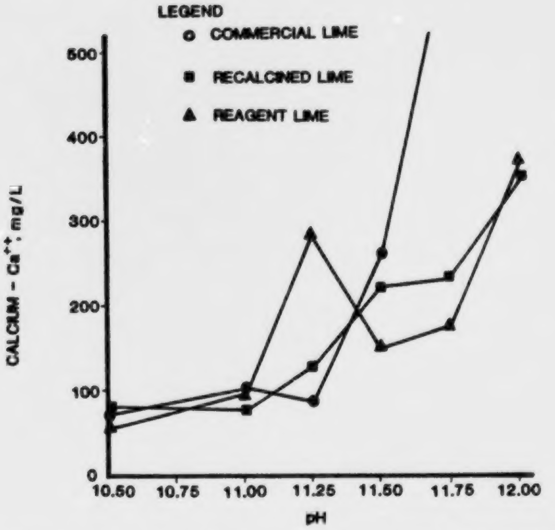


FIGURE 30. CALCIUM SOLUBILITY AS A FUNCTION OF pH FOR A FINISHED LOW ALKALINITY, HIGH MAGNESIUM LAKE WASHINGTON WATER TREATED BY 20 mg/L OF RECYCLED Mg^{++} AND COMMERCIAL, RECALCINED OR REAGENT LIME, SETTLING AND FILTRATION.

sites for organic interaction and better removal. However, the data presented indicate that there is little difference among the three lime sources. NaOH was used for pH control to determine the resulting effect on Mg^{++} and Ca^{++} residuals. The results of these tests are shown in Figures 31 and 32. Magnesium, as with lime, decreases from pH 11-11.5 to 1 mg/L or less. The calcium residual did not increase nearly as greatly as when lime was used for pH control, 50-70 mg/L versus over 300 mg/L. However, calcium does increase slightly at higher pH which was attributed to ion-pair or complex formation at the higher pH's. The much higher calcium residual is not surprising when $Ca(OH)_2$ is used for pH control, but the slightly increasing calcium residual when NaOH was used for pH control was unusual. Some of the $CaCO_3$ that had formed earlier at pH 9-10.5 was evidently not forming at pH's above 11.5. This may be due to extremely high organic content in Lake Washington water.

7.1.3 Mixing

Mixing during the rapid mix (coagulation) phase and the slow mix (flocculation) phase are important to the efficiency of any coagulation process. The effects of varying both slow and rapid mix mixing times for magnesium coagulation of the Lake Washington water are presented in Figures 33 through 36 for color, TOC and THMFP as well as turbidity removal. The primary objective was to construct isopleths from laboratory data for color, TOC and THMFP removal under varying mixing conditions. The rapid mixing and slow mixing times used in the earlier jar tests were identical to those in the Melbourne plant, 0.75 minutes in rapid mix and 19.0 minutes in slow mix. The samples were collected after 30 minutes of settling.

Two different magnesium doses were studied, zero (the optimum dose) and 9 mg/L of the saline recycled magnesium. The differences in color, TOC and THMFP removal during mixing were so slight that isopleth construction was not feasible. Instead the color, TOC and THMFP remaining after coagulation are documented as a function of both rapid and slow mixing times. As is seen in Figure 33, neither variations in rapid or slow mix affected the color removed. The minimum rapid and slow mixing times of 0.75 and 5.0 minutes resulted in a color residual of 12 and 11 cpu's for zero and 9 mg/L Mg^{++}. The maximum rapid and slow mixing times of 15 and 60 minutes resulted in a color residual of 10 and 9 cpu's for the same magnesium doses. Moreover, the color residuals are virtually the same for all data points in Figure 33.

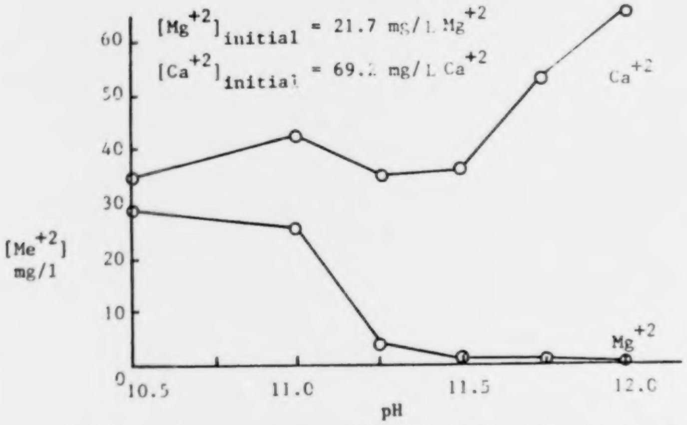


Fig. 31. Magnesium and calcium residuals for a low color, high magnesium Lake Washington water treated by coagulation of natural magnesium using NaOH for pH adjustment.

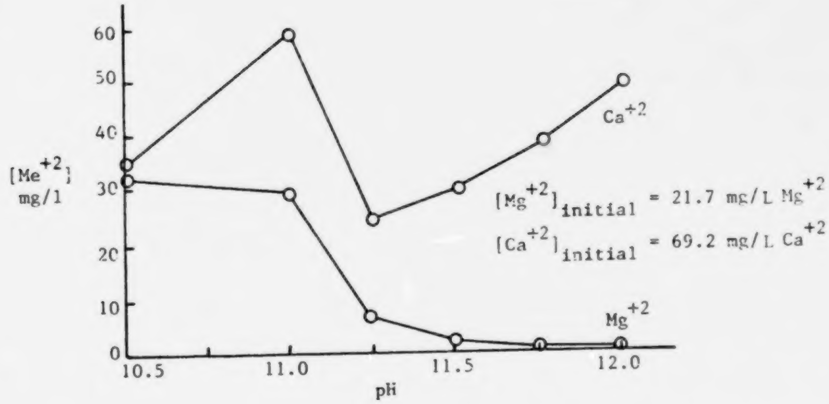


Fig. 32. Magnesium and calcium residuals for a low color, high magnesium Lake Washington water treated by coagulation with 9 mg/L Mg^{+2} of recycle magnesium and sodium hydroxide.

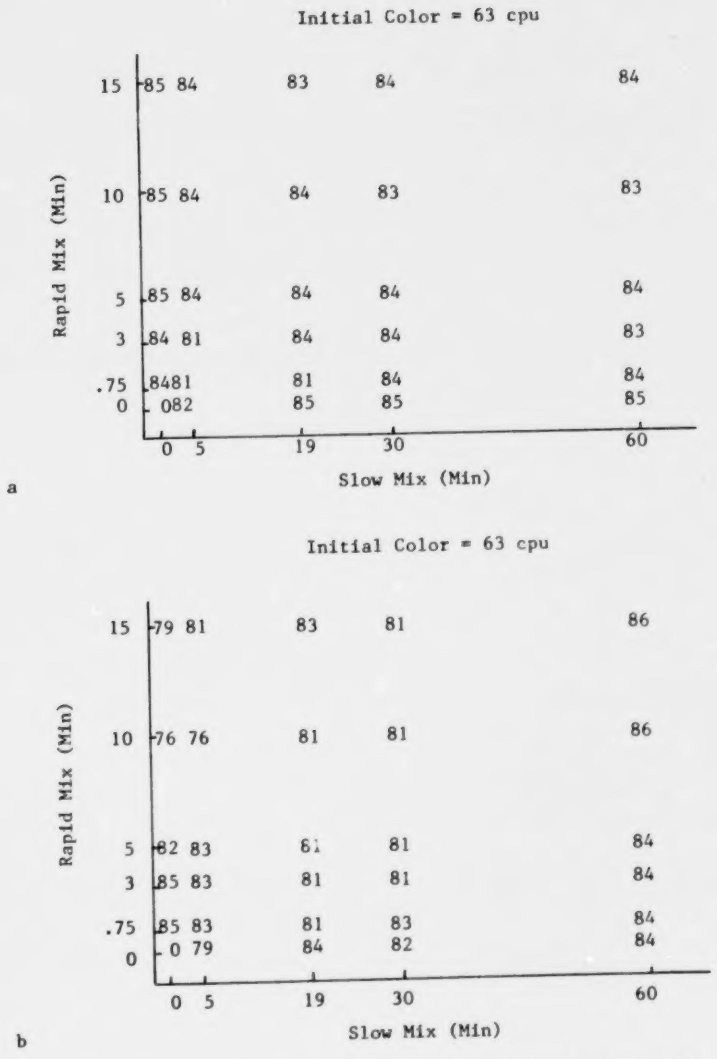


Fig. 33. Percent color removal as a function of variations in mixing times for low color, high magnesium Lake Washington water treated by coagulation with saline recycle magnesium doses of (a) 0 mg/L Mg^{+2} and (b) 9 mg/l Mg^{+2} and recalcined lime at pH 11.5. The magnesium concentration in the raw water was 18.3 mg/L Mg^{+2}. Saline $Mg(HCO_3)_2$ was utilized.

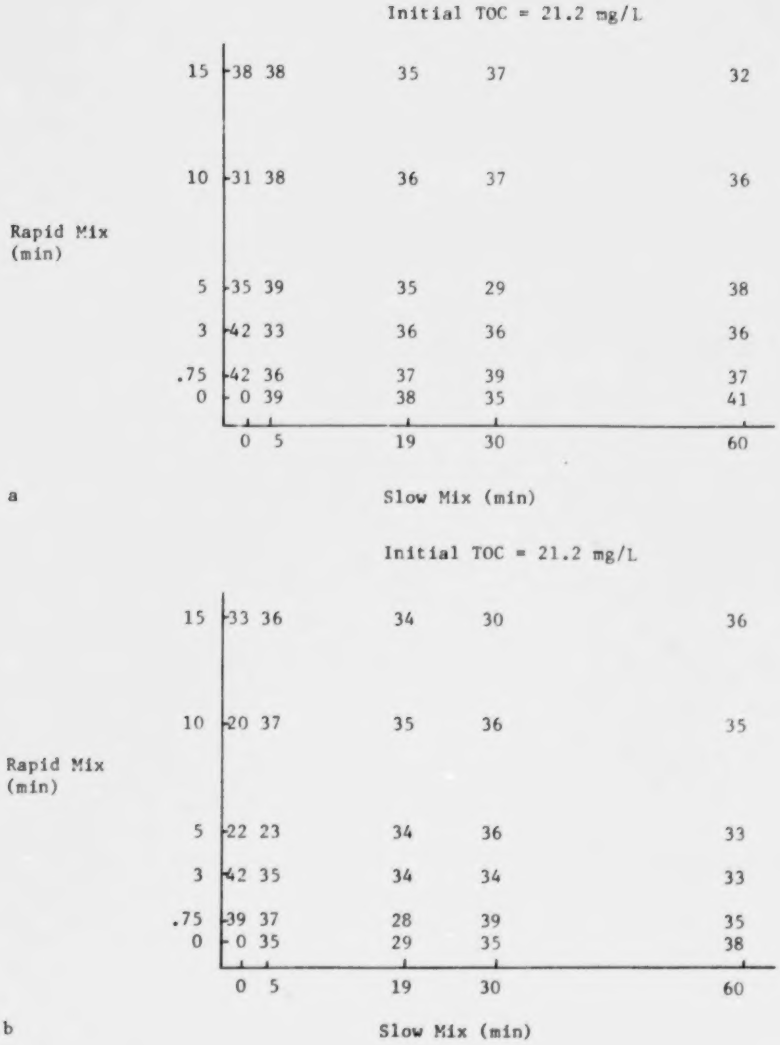


Fig. 34. Percent TOC removal as function of variations in mixing times for low color, high magnesium Lake Washington water treated by coagulation with saline recycle magnesium doses of (a) 0 mg/L Mg^{+2} and (b) 9 mg/L Mg^{+2} and recalcined lime at pH 11.5. The magnesium concentration in the raw water was 18.3 mg/L Mg^{+2}.

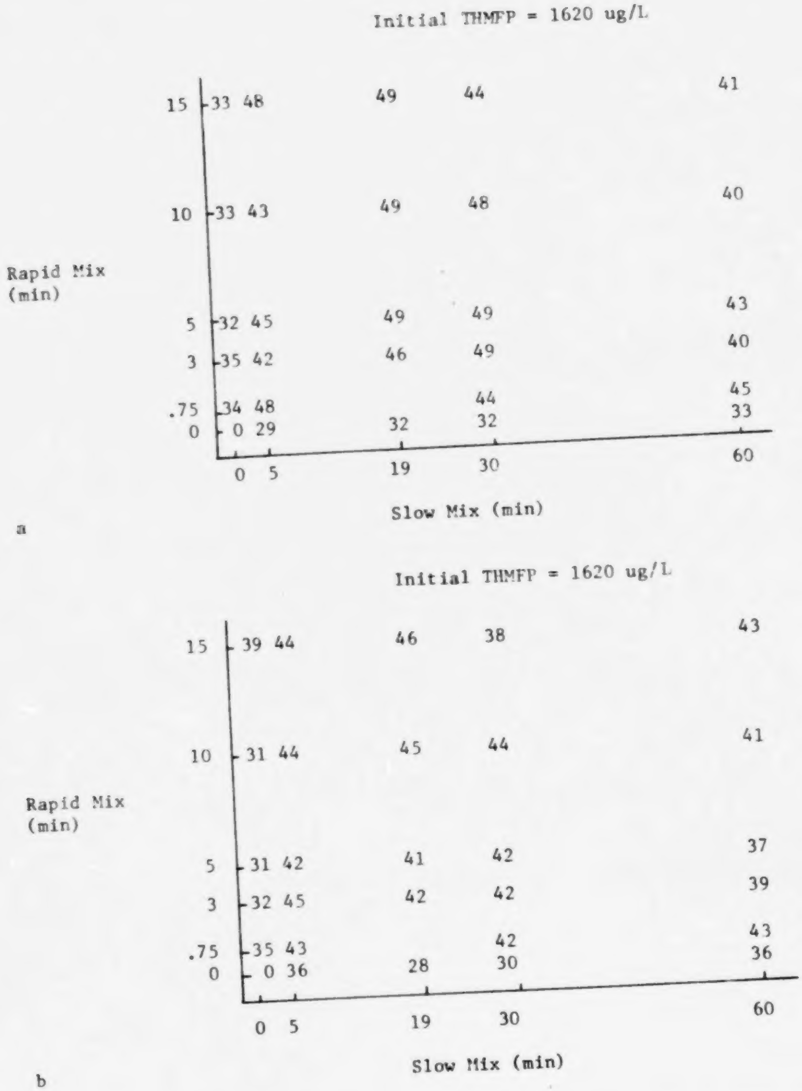


Fig. 35. Percent THMFP removal as a function of variations in mixing times for low color, high magnesium Lake Washington water treated by coagulation with saline recycle magnesium doses of (a) 0 mg/L Mg^{+2} and (b) 9 mg/L Mg^{+2} and recalcined lime at pH 11.5. The magnesium concentration in the raw water was 18.3 mg/L Mg^{+2}.

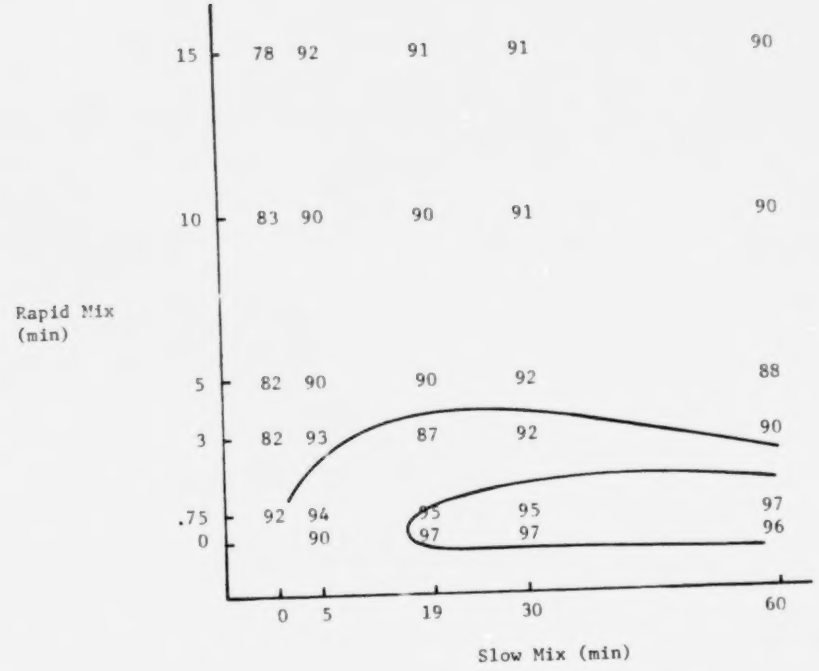


Fig. 36. Isopleth for percent turibidity removal as a function of variations in mixing times for a low color, high magnesium Lake Washington water treated by magnesium coagulation at a pH of 11.5 using recalcined lime. Settling time was 10 minutes, and magnesium concentration in the raw water was 18.3 mg/l Mg^{+2} and was only magnesium used as coagulant.

This same lack of mixing effect is seen again in Figures 34 and 35 for TOC and THMFP removal. There are approximately 12 to 13 mg/L TOC remaining for either magnesium dose equivalent to 35% TOC removal. There is no pattern for any variation in mixing times in either Figure 34 or 35. The THMFP removal data is more variable, indicating 42 to 53% THMFP reduction. However, there is no pattern to THMFP remaining, only more variation. It is noteworthy that very small doses of recycle magnesium do not adversely impact finished water color, TOC and THMFP. This may be significant when the magnesium content drops in the wet season by providing a magnesium source for better coagulation.

The conjunctive opportunities and velocity gradients were calculated by Equations 2 and 3 for the Phipps and Byrd jar test machine and are presented in Table 23. The range of rapid and slow mixing times investigated provides conjunctive opportunities within the range recommended for rapid and slow mixing.

$$G = (P/Cu)^{0.5} \tag{2}$$

$$Gt_d = (PC/u)^{0.5} Q^{-1} \tag{3}$$

where

G = velocity gradient (seconds^{-1})

t_d = mixing time (seconds)

Gt_d = conjunctive opportunities

P = power input (horsepower)

C = fluid volume (ft^3)

u = proportionality factor

Q = flow rate (mgd)

The data presented in Figure 36 shows the turbidity removal as a function of rapid or slow mixing times. Turbidity removal is observed to be minimized for a rapid mixing time of 0.75 minutes and a slow mixing time of 19 to 60 minutes. This is contrary to the color, TOC or THMFP data presented earlier. This is because the color, TOC and THMFP data were collected after coagulation, settling and filtration, whereas only coagulation and settling were involved for turbidity removal. This indicates the color, TOC and THMFP removal reactions are instantaneous during coagulation and not directly

TABLE 23

VALUES OF VELOCITY GRADIENT, G, AND CONJUNCTION OPPORTUNITY FOR JAR TESTS (WITH A PHIPPS AND BYRD JAR TEST MACHINE) TO DETERMINE THE EFFECT OF MIXING ON THMFP, TOC AND COLOR REDUCTION DURING MAGNESIUM COAGULATION

Rapid Mix				Slow Mix			
Time (min)	W (rpm)	G (sec^{-1})	Gt_d	Time (min)	W (rpm)	G (sec^{-1})	Gt_d
0.75	140	126	5,674	5.	35	16	4,725
3.	140	126	22,698	19.	35	16	12,955
5.	140	126	37,830	30.	35	16	28,350
10.	140	126	75,600	60.	35	16	56,700
15.	140	126	113,490				

affected by other than a minimum amount of mixing. However, floc sedimentation is affected by both rapid and slow mixing and could be improved if proper mixing conditions were determined and used. This data suggests that a short as possible rapid mix time is best for turbidity removal. The impact on plant operations would be first noticed as shorter filter runs. This could affect color, TOC and THMFP if a filter breakthrough occurred due to excessive floc carryover as indicated by turbidity from the clarifier due to poor settling.

Data presented in Figures 33, 34, 35 and 36 essentially indicate little variability in removal with mixing time, although there is a dip in TOC removal for rapid mix time of 5 or 10 minutes. If the data in Figures 33, 34, 35 and 36 are transposed to become isopleth lines for constant removal, the lines would all rise very abruptly a short distance from zero time to approximately 80% color, 40% TOC and 45% THMFP removal. From there the lines would proceed horizontally through the remainder of the data points. The main finding in the mixing work is that although color, TOC and THMFP are not affected by normal mixing time variations, floc formation and sedimentation are. Therefore, it can be concluded that the color, TOC and THMFP coagulation reaction is instantaneous, but that the rate controlling step in the coagulation process may well be sedimentation.

7.1.4 Polymers

The only polymer investigated was alum, $Al_2SO_4 \cdot 14H_2O$, which has been added to the rapid mix tank periodically at Melbourne. As is well known, the optimum range of $Al(OH)_3$ insolubility is pH 5 to 6. However, $Al(OH)_3$ can form the anionic species, $Al(OH)_4^-$, at pH 8 and higher.

This phenomenon has been responsible for turbidity restabilization and has required upper pH control in some cases when alum is used as a coagulant. It would be normally expected that alum would be soluble at pH's 11 to 11.5 as used in the magnesium process. The allowable thermodynamic solubility of $Al(OH)_4^-$ is approximately 500 mg/L as Al^{+3} in this pH range; therefore, it would not appear to be potentially effective as a polymer and would give high Al^{+3} concentrations in the finished water.

The data presented in Figure 37 show that alum at high pH's can be very effective as a coagulation aid for increasing color, TOC and THMFP removal during magnesium coagulation. The data in Figure 37 appear to obey a first

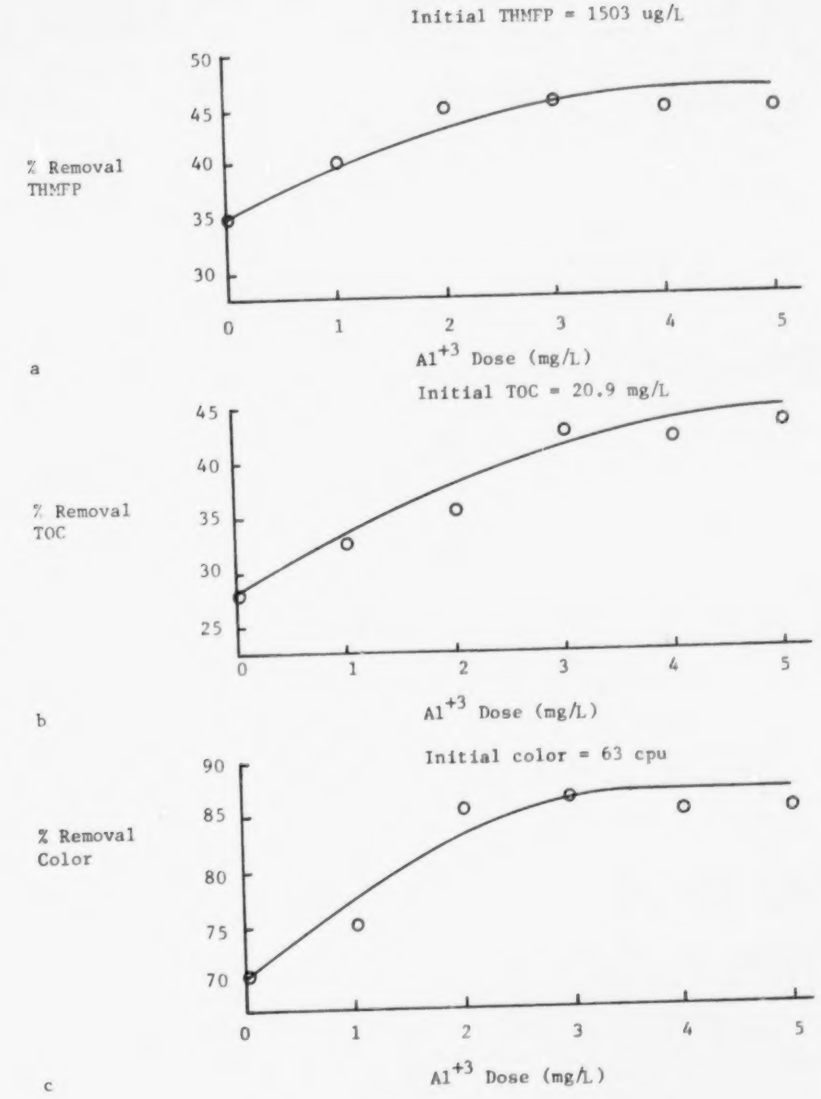


Fig. 37. Relationship between alum dose applied and percent removal of (a) THMFP, (c) TOC, and (c) color for a low color, high magnesium Lake Washington water treated by coagulation with recalcined lime at pH 11.5. Magnesium concentration in the raw water was 21 mg/L Mg^{+2}.

order response for the fraction of color, TOC and THMFP removed. The initial color, TOC and THMFP were slightly lower than had been experienced earlier, but good removals were obtained as alum dose was increased. The results shown in Figure 38 indicate alum increased floc settling velocity. The floc settling velocity lines are drawn for alum doses of 0, 2 and 3 mg/L Al^{+3} and would indicate an optimum dose of 2 mg/L Al^{+3}, as that is the bottom line representing minimum turbidity residual. However, the data for 5 mg/L Al^{+3} was not included in Figure 38 for clarity, as they were not distinguishable from the 2 mg/L Al^{+3} line.

It can be concluded that alum does promote floc sedimentation and optimum color, TOC and THMFP removal during coagulation. It was also found that Al^{+3} from alum as a polymer did not appear in the finished water until after a 2 mg/L Al^{+3} dose (about 22 mg/L as Alum) had been utilized. It was also noted that for the alum doses investigated, the ratio of moles Al^{+3} dosed to moles Al^{+3} leaving in the finished water was 3 to 1. It is possible that the negatively charged $Al(OH)_4^-$ polymer could stoichiometrically react with the positively charged magnesium floc and be removed from solutions for small alum doses. It is noteworthy that alum can promote organic removal and settling during coagulation, while not increasing the Al^{+3} residual in the finished water even though pH is out of the normal pH range of $Al(OH)_3$ insolubility.

The data presented in Figure 39 were selected at random from the jar test results. They indicate that not all of the THMFP precursors or TOC produce color. The THMFP intercept is approximately 800 μg/L at zero color for the treated water. The TOC intercept is about 4 mg/L at zero color. Likewise not all of the TOC produces a THMFP. The TOC intercept relative to THMFP is approximately 4 mg/L. These are linear projections and should not be interpreted exactly but the indicated relationships are logical for natural waters. That is, not all TOC will produce THMFP, and not all THMFP or TOC is produced by color-producing molecules, although a stoichiometric relationship may exist.

7.1.5 Jar Test Summary

The isopleths created from the Jar Tests demonstrated that an increase in coagulation pH always increased THMFP, TOC or color removal. When recycled $Mg(HCO_3)_2$ was prepared by enriching clarifier sludge with high magnesium saline well water, an increase in coagulant dose decreased the removal of

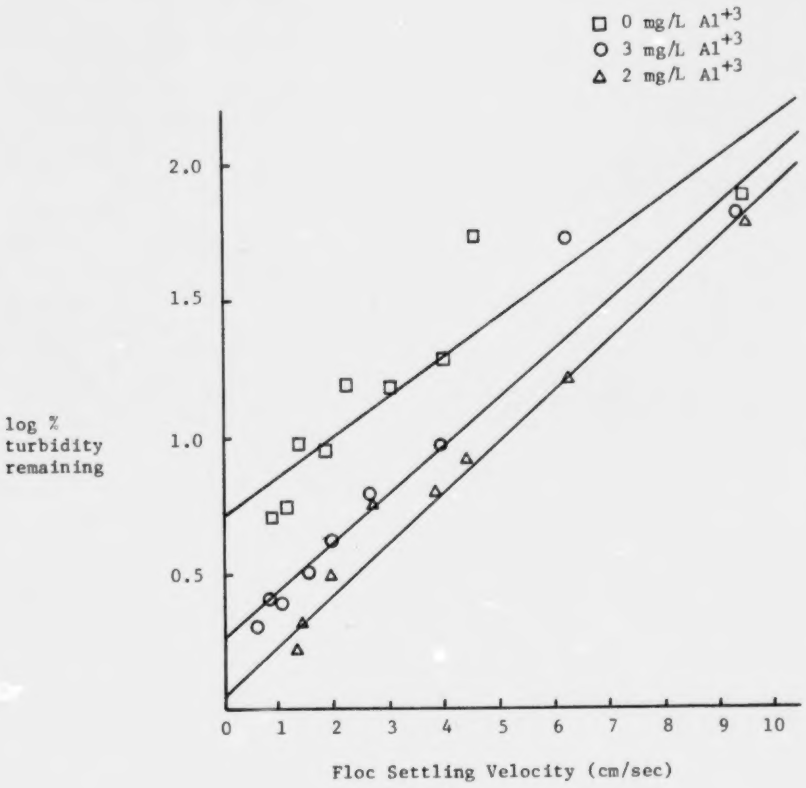


Fig. 38. Settling velocity distribution curves for a low color, high magnesium Lake Washington water treated by coagulation with recalcined lime at pH 11.5. Magnesium concentration in the raw water was 21 mg/L Mg^{+2}.

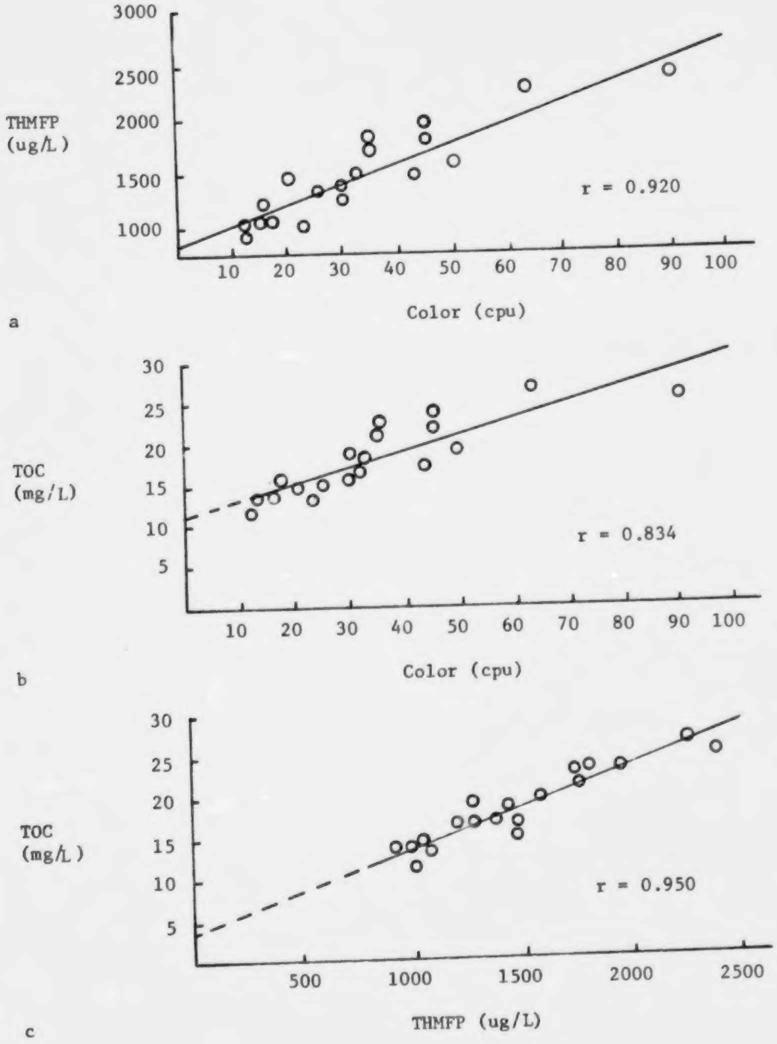


Fig. 39. Relationship between (a) THMFP and color, (b) TOC and color and (c) THMFP and TOC for Lake Washington water treated by magnesium coagulation, sedimentation and filtration at pH 11.5.

THMFP, TOC or color. However when recycled $Mg(HCO_3)_2$ was prepared in the conventional manner by direct carbonation of clarifier sludge, an increase in coagulant dose increased the THMFP, TOC and color removal. Conventionally prepared $Mg(HCO_3)_2$ did not remove as much THMFP, TOC and color as did fresh $MgSO_4 \cdot 7H_2O$.

The coagulant was recommended to be dosed in a range of 1 mg/L Mg^{++} for every 5 cpu (maximum) to every 10 cpu (minimum) of color. The recommended coagulant pH was 11.5 although approximately a 1.5% to 2% more THMFP, TOC and color removal was gained for every 0.1 pH unit increase from pH 11 to pH 12. A reduction of 80%-94% color, 40%-62% TOC and 25%-50% THMFP removal could be realized during coagulation in the treated water until after 2 to 3 mg/L Al^{+3} in the form of alum had been dosed. The THMFP or TOC or color removed during coagulation exhibited a stoichiometric relationship with coagulant dose. All color was indicated to be organic. All TOC did not produce THMFP. All THMFP was not produced from color producing molecules.

7.2 Recycle Recovery

The purpose of the Recycle Recovery Subtask was to investigate methods of purifying the recycle magnesium supernatant. All InstTHM's in this phase were zero, so that TermTHM equaled THMFP. This phase involved using chlorine dioxide and ozone to determine the effect of these oxidants on the residual color, TOC and THMFP of the recycled $Mg(HCO_3)_2$ coagulant, and then using this oxidized recycle $Mg(HCO_3)_2$ as a coagulant. The color, TOC and THMFP data for finished waters dosed identically with oxidized recycle $Mg(HCO_3)_2$ and unoxidized recycle $Mg(HCO_3)_2$ were compared, and the impact of oxidation on the recycled coagulant was evaluated. Previous recycle recovery work was conducted by Gill (1980) by passing the recycled $Mg(HCO_3)_2$ through a granular activated carbon column at various pH's and monitoring the color, TOC and THMFP of the filtered $Mg(HCO_3)_2$. This GAC filtered recycled $Mg(HCO_3)_2$ was used as a coagulant. The residual color, TOC and THMFP were compared to those from finished water prepared with recycled $Mg(HCO_3)_2$ coagulant that had not been filtered by GAC. As mentioned in the literature review section, the use of GAC did not improve the ability of recycle $Mg(HCO_3)_2$ to remove color, TOC or THMFP from the raw water.

The residual color, TOC and THMFP concentrations of the recycled $Mg(HCO_3)_2$ coagulant were quite high and variable. The $Mg(OH)_2$ floc was converted to $Mg(HCO_3)_2$ by the aqueous CO_2 stream, which also regulated the pH to approximately 7.3. The color, TOC and THMFP of the recycled magnesium varied from 3000 to 35000 cpu, 300 to 900 mg/L and 10000 to 100000 µg/L. The reason for the variation was the intermittent use of CO_2 in the magnesium recovery cell operation. The cell was used as a detention tank whether or not CO_2 was used so the carbonated liquor was flushed out periodically, which dropped the color, TOC and THMFP. The ultimate color, TOC and THMFP were not reached in the cell which indicates that organic equilibrium during magnesium recovery was not reached.

7.2.1 Recycle Recovery Oxidation

The effect of ozonation on the recycled $Mg(HCO_3)_2$ is shown in Tables 24 and 25. The initial color ranged from 2830 to 4950 cpu for the three samples and had to be measured by dilution. Ozonation of recycle magnesium reduced the color only when the heaviest O_3 dose, 420 mg/L, was used. The resulting color reduction was 40%, 1340 cpu or 3.19 cpu/mg O_3 utilized. This data indicates massive doses of O_3 would have to be utilized to reduce recycle color. Likewise, ozone was seen to have a limited affect on TOC or THMFP. The data in Tables 24 and 25 show percentage of change for color, TOC or THMFP for ozonated recycle magnesium. The only significant changes are for the THMFP of the ozonated recycle samples. However, measurement of THMFP requires dilution and is inherently variable because of dilution and the THMFP analysis. The implication of the results in Tables 24 and 25 is that ozone does not effectively reduce color, TOC or THMFP of the recycle magnesium. The same tests were conducted using ClO_2 instead of O_3, and the results are presented in Table 26. The ClO_2 dose range was 0 to 10.0 mg/L. The data indicate that ClO_2, like O_3, does not effectively reduce the color, TOC and THMFP of the recycle $Mg(HCO_3)_2$. Again, the largest reduction is in THMFP (19%); however, the variability in the measurement of large THMFPs is shown by the 15% variability between two separate measurements of the raw recycle (shown as zero dose in Table 26).

Only the saline recycle $Mg(HCO_3)_2$ was pretreated by oxidation with O_3 or ClO_2 before reuse as a coagulant. The conventional recycle $Mg(HCO_3)_2$ was never oxidized and reused, because the recycle recovery phase was completed before the in-plant (saline) method of preparation was known to be detrimental

Table 24. The Effect of Ozonation on Color, TOC and THMFP on Recycle $Mg(HCO_3)_2$

Sample 1

O_3 Utilized (mg/L)	Color (CPU)	% Difference	TOC (mg/L)	% Difference	THMFP (µg/L)	% Difference
0	4950	---	745	---	58,903	---
2.5	5450	+10.1	602	-19.2	52,164	-11.4
4.0	5450	+10.1	528	-29.1	52,488	-10.9
8.4	4450	-10.1	652	-12.5	40,783	-30.8
21.6	4740	-4.2	---	---	54,377	-7.7

Sample 2

O_3 Utilized (mg/L)	Color (CPU)	% Difference	TOC (mg/L)	% Difference	THMFP (µg/L)	% Difference
0	3340	---	720	---	77,800	---
50.4	3430	+2.7	708	-1.7	75,400	-3.1
92.5	3250	-2.7	732	+1.7	81,000	4.1
420	2000	-40.1	701	-2.6	69,500	-10.7

Table 25. TOC, Color and THMFP in Recycled $Mg(HCO_3)_2$ Treated with Ozone

Sample 3

O_3 Dose (mg/L)	TOC (mg/L) Initial	TOC (mg/L) Final	% Difference	pH Initial	pH Final	Color Initial	Color Final	% Difference	THMFP (µg/L) Initial	THMFP (µg/L) Final	% Difference
0	549	531	-3.3	8.45	8.71	2830	2830	-0.4	50,800	47,800	-5.8
1.9	565	563	-0.4	8.48	8.75	2730	2770	+1.5	50,800	39,500	-22.2
4.7	567	559	-1.4	8.48	8.75	2830	2770	-2.1	49,200	37,300	-24.2
7.0	547	558	+2.0	8.46	8.74	2830	2770	-2.1	47,600	45,500	-4.4
8.3	545	559	+2.5	8.46	8.78	2730	2770	+1.5	53,900	36,100	-32.9
10.7	548	545	-0.5	8.46	8.76	2830	2720	-3.9	52,500	42,100	-19.2

Table 26. TOC, Color and THMFP in Recycled Magnesium Supernatant Treated with ClO_2.

Sample 3

ClO_2 Dose (mg/L)	TOC (mg/L) Initial	TOC (mg/L) Final	% Difference	pH Initial	pH Final	Color Initial	Color Final	% Difference	THMFP (µg/L) Initial	THMFP (µg/L) Final	% Difference
0	521	511	-2	8.0	8.0	3600	3600	0	48,000	41,000	-15
0.5	524	528	0	9.0	8.05	3650	3800	+4	40,000	35,000	-13
1.0	519	511	-2	8.0	8.0	3600	3700	+3	46,000	44,000	- 4
2.0	517	522	1	8.0	7.95	3600	3750	+4	43,000	41,000	- 5
5.0	516	516	0	8.05	8.05	3650	3750	+4	43,000	41,000	- 5
10.0	520	520	0	8.0	8.05	3650	3800	+4	43,000	35,000	-19

to reuse. The recycled $Mg(HCO_3)_2$ prepared in the conventional manner in the laboratory was found to provide beneficial treatment for the high color water. However, this was initially attributed to the high color of the water instead of the in-plant method of preparation. Finally when the extensive studies in the plant evaluation were conducted and continuous beneficial treatment was observed, the effect of the in-plant preparation became obvious, but the recycle recovery and oxidation phases had been completed.

7.2.2 Recycle Reuse

The oxidized saline recycle magnesium was used as a coagulant to determine if the finished water color, TOC or THMFP would be effectively reduced, relative to the water quality resulting from treatment with unoxidized saline recycle $Mg(HCO_3)_2$. This data is presented in Tables 27, 28, and 29 for the raw water samples treated with ozonated recycle and in Table 30 for samples treated with ClO_2 recycle magnesium. The data in Table 27 show the use of ozonated saline recycle magnesium, as with saline recycle magnesium, increases the color, TOC and THMFP residual as the dose is increased. There is a deviation to this general trend for the THMFP by the 10.7 mg/L O_3 sample, which is contrary to the large color and TOC increases at that O_3 dose. The positive values in the % difference columns of Table 27 indicate ozonated saline recycled magnesium will degrade finished water quality relative to samples prepared by coagulation at pH 11.5 with lime only. The data in Tables 28 and 29 are more variable but definitely show no improvement in color, TOC or THMFP when comparing samples coagulated with ozonated saline recycled magnesium versus samples prepared with zero dose recycled magnesium.

The quality of ClO_2 saline recycle treated samples is presented in Table 30. The % difference columns of this table show the percentage of change in color, TOC and THMFP of the samples prepared with ClO_2 saline recycle versus those prepared with zero recycle dose. The positive signs in these columns indicate less effective treatment by the ClO_2 saline recycle and negative signs indicate more effective treatment. The data presented in Table 30 indicate that ClO_2 oxidation of the recycle $Mg(HCO_3)_2$ has little, if any, effect on the finished water. There are about as many positive changes as negative changes in final water quality. The largest change in color is 8 cpu, in TOC is 1.16 mg/L and in THMFP is 364 μg/L. These changes are small with respect to this water.

Table 27. Finished Water Quality using Ozone-Treated Saline Recycled Magnesium and Lime for Coagulation and pH Control - Raw Water Sample #1.

Mg^{++} Dosage (mg/L)	O_3 Dosage (mg/L)	pH	Color (cpu)	% Difference	TOC (mg/L)	% Difference	THMFP (μg/L)	% Difference
0	0	7.6	65		20.1		1207	
0	0	11.5	17		13.2		265	
10	0	11.5	22*		15.8*		484*	
10	1.9	11.5	27	+22.7	14.9	-5.5	631	+30.4
10	4.7	11.5	27	+22.7	15.2	-3.4	496	+2.5
10	7.0	11.5	27	+22.7	15.2	-3.4	858	+77.3
10	10.7	11.5	32	+45.5	15.8	+0.3	241	-50.2
15	0	11.5	22*		15.5*		729*	
15	1.9	11.5	27	+22.7	16.3	+4.7	968	+32.8
15	4.7	11.5	27	+22.7	16.7	+7.3	680	-6.7
15	7.0	11.5	32	+45.5	16.3	+5.2	1066	+46.2
15	10.7	11.5	27	+22.7	16.4	+5.7	674	-7.5
20	0	11.5	27*		17.0*		827*	
20	1.9	11.5	27	0	17.2	+1.3	1023	+23.7
20	4.7	11.5	27	0	16.8	-1.3	913	+10.4
20	7.0	11.5	32	+18.5	16.9	-0.3	1121	+35.6
20	10.7	11.5	32	+18.5	16.2	-4.3	1023	+23.7

*Control values for the individual Mg^{++} dosages.

Table 28. Finished Water Quality Using Ozone-Treated Saline Recycled Magnesium and Lime for Coagulation and pH Control - Raw Water Sample #2

Mg^{++} Dosage (mg/L)	O_3 Dosage (mg/L)	pH	Color (cpu)	% Difference	TOC (mg/L)	% Difference	THMFP (μg/L)	% Difference
0	0	11.5	13		15.1		1020	
10	0	11.5	15*		15.6*		980*	
10	50.4	11.5	15	0	15.7	+1.0	985	+0.5
10	92.5	11.5	20	+33.3	15.7	+0.6	710	-27.6
10	420	11.5	15	0	15.5	-0.3	1020	+4.8
15	0	11.5	15*		16.0*		974*	
15	50.4	11.5	15	0	15.9	-0.6	996	+2.3
15	92.5	11.5	20	+33.3	15.8	-1.3	476	-51.1
15	420	11.5	15	0	18.0	+12.5	1123	+15.3
20	0	11.5	20*		16.6*		1088*	
20	50.4	11.5	15	-25.5	16.9	+1.6	778	-28.5
20	92.5	11.5	30	+50.0	16.0	-3.7	904	-16.9
20	420	11.5	20	0	17.5	+5.7	1123	+3.2

*Control values for the individual Mg^{++} dosages

Table. 29 Finished Water Quality Using Ozone-Treated Saline Recycled Magnesium and Lime for Coagulation and pH Control - Raw Water Sample #3

Mg^{++} Dosage (mg/L)	O_3 Dosage (mg/L)	pH	Color (cpu)	% Difference	TOC (mg/L)	% Difference	THMFP (µg/L)	% Difference
0	0	11.5	23*		15.9*		168*	
10	2.5	11.5	18	-21.7	13.8	-13.2	676	+302
10	4.0	11.5	23	0	13.1	-17.6	647	+285
10	8.4	11.5	23	0	12.6	-20.8	491	+192
15	2.5	11.5	18	-21.7	13.6	-14.5	1072	+538
15	4.0	11.5	23	0	12.4	-22.0	702	+318
15	8.4	11.5	18	-21.7	13.4	-15.7	652	+288
20	2.5	11.5	18	-21.7	15.5	-2.5	805	+379
20	4.0	11.5	23	0	13.5	-15.1	642	+282
20	8.4	11.5	23	0	14.1	-11.3	960	+471

*Control values

Table 30. Finished Water Quality Using Chlorine Dioxide-Treated (Saline) Recycled Magnesium and Lime for Coagulation and pH Control Raw Water Sample #4.

Mg^{++} Dosage (mg/L)	ClO_2 Dosage (mg/L)	pH	Color (cpu)	% Difference	TOC (mg/L)	% Difference	THMFP (μg/L)	% Difference
0	0.0	7.5	65		22.7		1580	
0	0.0	11.5	13		13.2		844	
10	0	11.5	10*		13.2*		1052*	
10	0.5	11.5	18	+80.0	14.4	+8.8	1109	+5.4
10	1.0	11.5	10	0	14.1	+6.7	980	-6.8
10	2.0	11.5	10	0	13.7	+3.3		
10	5.0	11.5	13	+30.0	13.1	-0.8	931	-11.5
10	10.0	11.5	10	0	13.4	+6.9	1052	0
15	0.	11.5	10*		14.7*		1037*	
15	0.5	11.5	13	+30.0	13.9	-5.3	931	-10.2
15	1.0	11.5	16	+60.0	13.4	-9.0	1109	+6.9
15	2.0	11.5	13	+30.0	13.6	-7.1	989	-4.6
15	5.0	11.5	13	+30.0	13.6	-7.7	1037	0
15	10.0	11.5	12	+20.0	13.4	-8.5	1037	0
20	0	11.5	13*		13.5*		989*	
20	0.5	11.5	13	0	13.8	+2.4	1052	+6.4
20	1.0	11.5	18	+38.5	13.4	-0.7	1124	+13.7
20	2.0	11.5	10	-23.1	14.6	+8.5	859	-13.1
20	5.0	11.5	13	0	13.3	-1.3	965	-2.4
20	10.0	11.5	10	-23.1	13.9	+3.2	1345	+36.0

*Control values for individual Mg^{++} dosages.

It is unfortunate that the recycled $Mg(HCO_3)_2$ was made saline by plant preparation. However, it is obvious that oxidation of the saline recycle was not beneficial to treatment. It is probable that such high doses of either ClO_2 or O_3 would be required to have any effect on recycled $Mg(HCO_3)_2$ that the oxidation of conventional recycle $Mg(HCO_3)_2$ would be uneconomical and questionable as to its effect.

7.2.3 Recycle Summary

Neither O_3 or ClO_2 oxidation effectively improved the ability of the saline recycled $Mg(HCO_3)_2$ coagulant to remove more THMFP, TOC or color from the raw water. These oxidants were only applied to saline recycle $Mg(HCO_3)_2$, but would not be expected to affect the capability of conventionally prepared $Mg(HCO_3)_2$ recycle based on these results.

7.3 Oxidation

The Oxidation Phase consisted of using ozone and chlorine dioxide to treat the raw or finished water to reduce THMFP. In this phase all InstTHM's were zero so that TermTHM equaled THMFP. The color and TOC residuals were also monitored during oxidation. The work done by Kimes described in Chapter 4 is pertinent to this section. Kimes' work was initiated after the proposal for Melbourne was sent to EPA but before funds were received for the project. Kimes' work investigated the effect of ozone on only the THMFP and color of the raw or coagulated Lake Washington water. The Oxidation Phase involved two oxidants, ClO_2 and O_3, and the effect on THMFP, TOC and color of the finished water after oxidation separately of the raw water, of the treated water after coagulation at pH 11.5 and after recarbonation at pH 8.3. Kimes' work is only similar to the project oxidation work after recarbonation but is discussed here because ozone was used on the same water with similar results. These experiments were done in three separate but identical studies to gain statistical validity. The effect of ozone utilized by both finished and raw water is shown in Figures 4 and 5 for the second study only and is very similar to results from the third and first studies. The data from each study was plotted as THMFP versus time and utilized ozone to show maximum THMFP yield and the slopes of the THMFP versus utilized ozone lines.

A chlorine dose of 25 to 50 mg/L and 15 to 30 mg/L was used for the raw and finished water samples. The pH of the raw water (7.2 - 7.6) was not adjusted but the finished water pH was adjusted to 7.6 before chlorination.

The maximum O_3 dose utilized was 10.6 mg/L for the raw water and 5.3 mg/L for the finished water. In the first study, the THMFP reached maximum yield at 700 μg/L for the finished water and 1400 μg/L for the raw. There was a free chlorine residual after 48 hours but it was less than 1.0 mg/L. The initial chlorine dose was 25 mg/L for the raw and 15 mg/L for the finished water samples. A temperature of 20°-22°C was utilized for THMFP. When these studies were repeated, the chlorine dose was increased to 50 mg/L for the raw and 25 mg/L for the finished water samples. The chlorine residual was greater than 1.0 mg/L after 96 hours in both the second and third studies. The THMFP yield is approximately 2800 μg/L for the raw and 1200 μg/L for the finished water samples. The growth of THMFP as shown in Figures 4 and 5 was still increasing at t = 96 hours.

The three studies utilized different water samples. TOC was not measured for this study because of instrument malfunction prior to the project start and eventual replacement. However, the data in the top half of Figure 4 indicate a larger chlorine dose produces a higher THMFP for the same time periods. This work was utilized to model the THMFP rate study for this project by considering chlorine dose as an independent variable in the development of a THMFP model.

Some of the THMFPs were observed to decrease slightly relative to the succeeding THMFP for the same ozone dose. Because there were so many data points and lines on Figure 4, the THMFP was plotted as a function of applied ozone as shown in Figure 5. These data show that ozone applied to the raw and finished Lake Washington water at pH 7.6 did not affect the THMFP. The same results were shown in both of Kimes' other studies which were completed after the EPA Melbourne project had been proposed.

7.3.1 Ozone

The data in Table 31 show the effects of ozonation of the raw water after coagulation, settling and filtration. The data in Table 31 show that an increase in utilized ozone dose will decrease color after coagulation. The unozonated raw water was reduced to a color of 25 cpu after coagulation. The maximum O_3 dose utilized, 34 mg/L, decreased the residual color to 11 cpus; an improvement of 14 cpu's over the unozonated raw water sample that received identical pretreatment except for O_3. However, no consistent effect of utilized O_3 on residual TOC or THMFP is observed in Table 31. The coagulation

Table 31. TOC, Color and THMFP for Ozonated Raw Water After Coagulation, Settling and Filtration (CSF)

TREATMENT	PRE-COAGULATION O_3 UTILIZED (mg/L)	TOC (mg/L)	% Difference	COLOR (cpu)	% Difference	THMFP (mg/L)	% Difference
None	0 (Raw)	24.1*		60*		1475*	
CSF		15.8		25		659	
Ozonation	1	25.0	+3.6	48	-20.0	1365	-7.5
Ozonation & CSF		17.1		15		505	
Ozonation	1.8	24.5	+1.5	48	-20.0	1217	-17.5
Ozonation & CSF		17.4		15		673	
Ozonation	8.6	23.7	-2.0	45	-25.5	1426	-3.3
Ozonation & CSF		16.2		12		440	
Ozonation	18.1	23.9	-1.2	40	-33.3	903	-38.8
Ozonation & CSF		16.3		11		517	
Ozonation	34	23.9	-0.9	35	-41.7	1106	-25.0
Ozonation & CSF		15.8		11		608	

*Control value

process is observed to reduce the TOC and THMFP of the raw water from 24.1 mg/L and 1475 μg/L to 15.8 mg/L to 659 μg/L. The TOC of the ozonated waters varies from 15.8 to 17.4 mg/L with no obvious correlation to O_3 dose. Likewise, the THMFP varies from 440 to 673 μg/L from the ozonated samples in Table 31 with no obvious correlation to O_3 dose.

The data in Table 32 show that ozonation at pH 11.5 does reduce color after coagulation, settling and filtration. A 1 mg/L dose of utilized ozone applied after coagulation, filtration and settling reduced the color to 5 cpus; whereas, when ozonation preceded coagulation, settling and filtration, the same O_3 dose only achieved a 10 cpu color residual. This trend is consistent for the color data in Tables 31 and 32 and demonstrates that ozonation for color removal would be more effective after coagulation, settling and filtration than before coagulation, settling and filtration. The use of O_3 after coagulation, filtration and settling at pH 11.5 did reduce both TOC and THMFP as shown in Table 32. The lowest TOC, 12.8 mg/L, and THMFP, 491 μg/L, residuals were achieved for the largest utilized ozone dose. In each sample in Table 32 where O_3 was applied, a drop in TOC and THMFP was observed for the ozonated samples relative to the unozonated samples, with the exception of the TOC data for 1 mg/L O_3 and the THMFP data for 206 mg/L O_3. However, ozone is costly at such high doses and the final THMFP is still in excess of 0.1 mg/L. It is possible that ozone could be effectively utilized at Melbourne after coagulation and settling at pH 11.5 for trace color removal. If ozonation were practiced at Melbourne, it would be possible to ozonate either the raw water (pH 7 - 8), the coagulated and settled water (pH 11.5) or the coagulated, settled, recarbonated and filtered water (pH 8 - 8.5). Our studies, considering the work of Kimes, indicate that ozonation at pH 11.5 after coagulation would be most effective.

7.3.2 Chlorine Dioxide

The effect of ClO_2 oxidation prior to coagulation on color, TOC and THMFP is shown before coagulation in Table 33, after coagulation at pH 8 in Table 34 and after coagulation and recarbonation at pH 11.5 in Table 35. ClO_2 was applied in doses to 10 mg/L. There is some question if ClO_2 could be used in doses greater than 2 mg/L anywhere in Florida because of potential health concerns by FDER. Consequently, because of cost and potential regulatory limitations on ClO_2, doses larger than 10 mg/L were not investigated.

Table 32. TOC, Color and THMFP For Coagulated, Settled and Filtered Water After Ozonation at pH 11.5

TREATMENT	POST-COAGULATION O_3 UTILIZED (mg/L)	TOC (mg/L)	% Difference	COLOR (cpu)	% Difference	THMFP (mg/L)	% Difference
None	0 (Raw)	24.1		60		1475	
Coagulation		15.8*		25*		659*	
Coagulation	1	16.4		15		601	
Coagulation & Ozone		17.0	+7.6	10	-60.0	529	-19.7
Coagulation	2	16.4		15		564	
Coagulation & Ozone		15.6	-1.3	8	-68.0	398	-39.6
Coagulation	4.9	16.9		12		766	
Coagulation & Ozone		14.4	-8.6	8	-68.0	597	-9.4
Coagulation	23.6	16.6		12		700	
Coagulation & Ozone		15.2	-4.0	5	-80.0	586	-11.1
Coagulation	117.8	16.7		11		706	
Coagulation & Ozone		13.7	-13.1	5	-80.0	550	-16.5
Coagulation	206	16.6		10		472	
Coagulation & Ozone		12.7	-19.3	5	-80.0	491	-25.5

*Control value

Table 33. TOC, Color and THMFP of the Raw and Coagulated-Filtered Samples Oxidized With ClO_2 Before Coagulation at pH 11.5.

	RAW			FILTERED		
ClO_2 mg/L	TOC mg/L	Color cpu	THMFP μg/L	TOC mg/L	Color cpu	THMFP μg/L
0	19.9	50	1084	13.7	10	776
1	19.4	45	1084	13.0	10	616
3	19.0	40	1953	12.9	10	556
5	19.3	30	1051	12.9	10	637
10	19.9	25	898	12.7	10	505

Table 34. TOC, Color and THMFP of Raw and Filtered Samples Oxidized With ClO_2 at pH 8.0 After Coagulation and Recarbonation.

Sample	ClO_2 mg/L	TOC mg/L	Color cpu	THMFP mg/L
Raw	0	28.9	150	1609
Filtered	0	20.4	35	851
Filtered	1	20.3	30	778
Filtered	3	21.0	35	870
Filtered	5	20.9	30	677
Filtered	10	21.6	10	659

Table 35. TOC, Color and THMFP of Raw and Filtered Samples Oxidized with ClO_2 After Coagulation at pH 11.5 and Then Carbonation to pH 8.0.

Sample	ClO_2 mg/L	TOC mg/L	Color cpu	THMFP mg/L
Raw	0	28.9	150	1609
Filtered	0	17.1	15	786
Filtered	1	16.9	15	741
Filtered	3	17.0	10	627
Filtered	5	16.9	10	664
Filtered	10	16.9	5	541

ClO_2 was observed to decrease the color of the raw water from 50 to 25 cpu as shown in Table 33. Approximately 3 to 5 cpu/mg/L ClO_2 were removed. There was no reduction in TOC and no apparent reduction in THMFP, although the raw water THMFP was reduced for the 10 mg/L ClO_2 dose. There is no consistent relationship between ClO_2 dose and THMFP reduction. Furthermore the reduction is less than the expected 20% variability for THMFP measurement as well as being inconsistent. The ClO_2 treated raw water samples were also coagulated and filtered, and the resulting color, TOC and THMFP were measured. These results are also shown in Table 33. These results show no effect on color remaining after coagulation but some reduction of THMFP and TOC. The color was 10 cpu after coagulation which is an 80% reduction and can be normally expected as shown by the section on jar tests. The TOC reduction is slight reaching a maximum of 1.0 mg/L or 7% at 10 mg/L ClO_2. The THMFP is significantly reduced at 10 mg/L ClO_2 by 271 μg/L or 35%. This could be because the organic precursors were oxidized by ClO_2 or the residual ClO_2 was reacting with the chlorine, reducing the THMFP.

The color, TOC and THMFP of ClO_2 treated samples at pH 8.0 after coagulation and recarbonation are shown in Table 34. TOC reduction is attributable to coagulation, not to ClO_2 oxidation. Coagulation here is by adjusting pH to 11.5 and precipitating the natural magnesium from the raw water which accounts for the low TOC removal of approximately 28%. Color is reduced by ClO_2, reaching a low of 10 cpu at a 10 mg/L ClO_2 dose for a 25 cpu reduction. The THMFP was reduced a maximum of 192 μg/L or 23% by a dose of 10 mg/L ClO_2. The trend of THMFP reduction is relatively constant with ClO_2 dose although the THMFP of the sample treated with 3 mg/L ClO_2 is high. However considering the variability of the THMFP measurement, the observation of a reduction in THMFP with increasing ClO_2 dose is valid.

Because magnesium precipitates at a high pH, the opportunity to use any oxidant at high pH is present. The effect of ClO_2 on color, TOC and THMFP is shown in Table 35 when dosed after coagulation at pH 11.5 before recarbonation. The data appear similar to the ClO_2 results when applied after recarbonation. That is little or no reduction in TOC (0.3 mg/L at a 10 mg/L ClO_2 dose), some reduction in color and THMFP (10 cpu and 245 μg/L at a 10 mg/L ClO_2 dose). These reductions are significant, 67% color and 23% THMFP, in light of the consistency of the data.

7.3.3 Oxidation Summary

In all the results of the oxidation phase, neither O_3 nor ClO_2 ever reduced the THMFP to the 0.1 mg/L regulation. However ClO_2 did consistently reduce THMFP, but an 80% or greater THMFP reduction would be required to meet the regulation. The data shown in Tables 33, 34, and 35 does not suggest that ClO_2 is more reactive at higher pH's as no benefit for color, TOC or THMFP reduction at different reaction pH's was apparent. Ozone did reduce color before and after coagulation, but only reduced the TOC at pH 11.5 after coagulation. If any oxidant is to be used at Melbourne, these data indicate it will be for color removal and would be effective.

7.4 Trihalomethane Formation Potential Model

In this phase InstTHM's were always zero, therefore TermTHM equaled THMFP. The purpose of this phase was to develop a statistical model that would be representative of the THMFP and could be used with some confidence to minimize THMFP by Melbourne and other potable water suppliers. The experimental design for the development of a model was based on observed reaction effects in the literature.

7.4.1 THM Reaction

The traditional haloform reaction is shown in equation (4) involving a methyl ketone, a halogen and a base.

$$aCH_3OCR + bCl_2 + cOH^- \rightarrow HCCl_3 + R\text{-}COO^- \qquad (4)$$

If this reaction is elementary and irreversible, the equation for the THMFP as a function of time can be written as shown in equation (5).

$$\frac{d(HCCl_3)}{dt} = k\ (CH_3OCR)^a(Cl_2)^b(OH^-)^c \qquad (5)$$

While methyl ketones may exist in drinking water, it is likely that many other organics also exist that contribute to THMFP and that TOC would be a better parameter to represent those precursors. It is also probable and has been shown that: (1) changes in TOC, chlorine dose, pH, temperature and time will affect the THMFP and if possible that (2) the effect of these variables on THMFP could be related by a statistically based model. Such a model is shown in equation (6) and this section summarizes these results for such a model.

$$THM = K(Cl)^a(T)^b(TOC)^c(OH)^d(t)^e \qquad (6)$$

where:

where:

THMFP = μmoles/L THM
Cl = mmols/L Cl
T = temperature °C
TOC = mmols/L TOC-C
OH = mmols/L OH^-
t = time-hours

K = coefficient
a = Cl exponent
b = temperature exponent
c = TOC exponent
d = OH exponent
e = time exponent

Consequently, a statistical study was initiated to determine the effect of chlorine dose, TOC, pH, temperature and time on THMFP. Three separate waters were chosen for these investigations on the basis of varying TOC. The first of these was a water taken from the South Water Treatment Plant in Melbourne, Fldorida which takes its water from Lake Washington, in the St. John's River. This is a potable water source that had an average TOC of 20 mg/L after treatment and serves 125,000 people. The second water utilized was taken from the Hillsborough Water Treatment Plant in Tampa, Florida. The Hillsborough plant treats 65 mgd, serves 500,000 people and has an average finished water TOC of 7-12 mg/L. The third water selected was the University of Central Florida's finished water. This water is taken from a shallow aquifer by wells 100 to 300 feet deep. The average TOC of this source is 2 to 3 mg/L.

7.4.2 Experimental Design

The experimental design is shown in Figure 40. Each water represents a variation for TOC. The reaction pH values investigated were 6, 7.5 and 9.0 and were selected to cover the majority of the finished potable waters. These pH's were continually maintained within ±0.15 of the designed pH from the beginning to the end of each experiment. Chlorination doses utilized were 0, 5, 10, 20 and 40 mg/L. The latter chlorine dose is high, but was required in order to maintain an excess of chlorine for the high TOC water during the reaction period. Reaction temperatures were 8°C, 16°C and 32°C in order to cover the temperature extremes common in Florida and national distribution systems. All reactions were executed in temperature-controlled environments with aqueous water temperatures regulated before reaction. The sample times were 0, 0.05, 1.0, 6.0, 24.0, 48.0 and 144.0 hours. One of every ten duplicate samples was carried completely through the experiment to document precision. EPA unknown samples from their performance evaluation program were

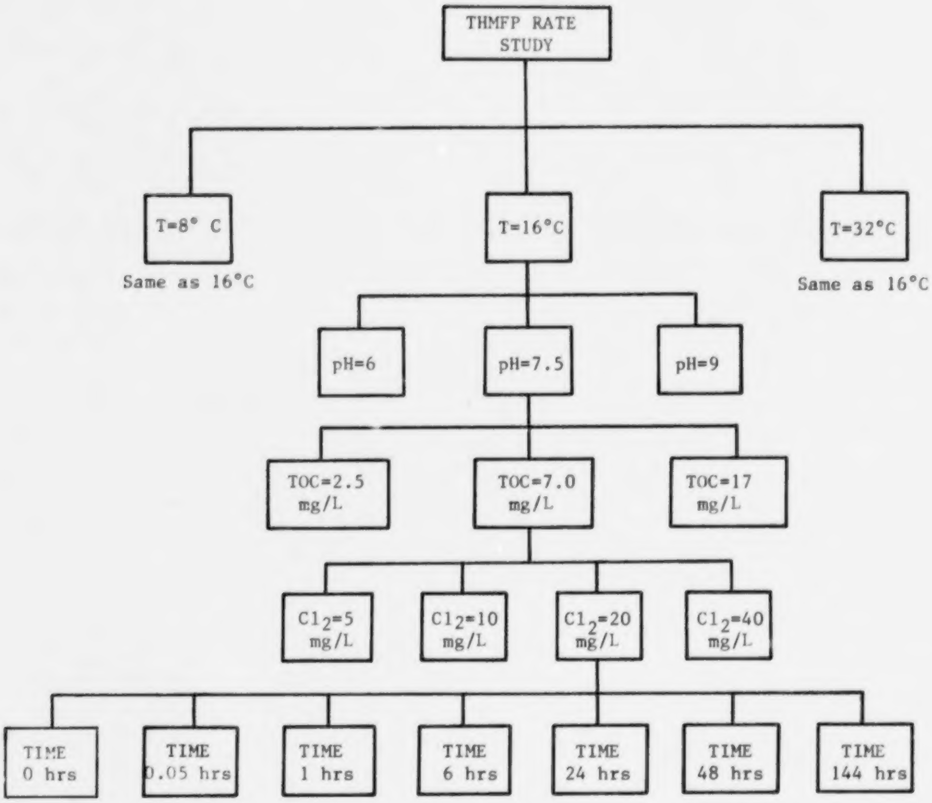

THMFP RATE STUDY
T=8° C
Same as 16°C
T=16°C
T=32°C
Same as 16°C
pH=6
pH=7.5
pH=9
TOC=2.5 mg/L
TOC=7.0 mg/L
TOC=17 mg/L
Cl2=5 mg/L
Cl2=10 mg/L
Cl2=20 mg/L
Cl2=40 mg/L
TIME 0 hrs
TIME 0.05 hrs
TIME 1 hrs
TIME 6 hrs
TIME 24 hrs
TIME 48 hrs
TIME 144 hrs

Fig. 40 Diagram for conducting THM formation rate study.

analyzed to document accuracy. Internal precision was ±7% and accuracy was within acceptable ranges as defined by EPA. Slightly over 600 separate samples of THMFP were analyzed for this study.

7.4.3 Model Development

The effects of changing each of the parameters investigated is shown in Figure 41. Figure 41a represents only the effect of increasing chlorine dose on THMFP at pH 6, 16.9 mg/L TOC and 8°C. Inspection of Figure 41a shows that a 5 mg/L chlorine dose formed 0.8 μmols/L THM's after 144 hours but that an increase in chlorine dose to 40 mg/L resulted in a THMFP of 5 umols/L for the same period. The average molecular weight for the THM's was approximately 127 with chloroform accounting for 85% of the THMFP which is approximately the same as has been found on a national basis. Free chlorine residual was monitored at all times with the exception of the 0.05 hour sample. The only difference between Figure 41a and Figure 41c is that the pH is increased from 6 to 9.2. TOC and temperature are the same; however, for a 10 mg/L chlorine dose, the THMFP after six hours is increased from 2.1 to 3.9 μmols/L. This increase is attributable to pH. If the TOC is decreased from 16.9 to 2.5 mg/L and all other parameters held constant as shown in Figure 41b relative to Figure 41a, inspection of the 6 hour - 10mg/L chlorine dose point on Figure 41b and Figure 41a reveals the lower TOC sample formed only 0.22 μmols/L as compared to 2.1 μmols/L for the higher TOC sample. Figure 41d represents a change in the reaction temperature for THMFP in the low TOC sample at pH 6, 10 mg/L Cl for 6 hours. The change in temperature from 8°C to 32°C increased the THMFP from 0.22 to 0.51 μmols/L. It should be noted that there was a change in the TOC from 2.5 to 3.2 mg/L due to variations in the source. However, Figure 41 indicates that THMFP will increase with time, temperature, TOC, chlorine dose and pH for the conditions of this study, and that statistical modeling of the data is feasible.

The results of this study were analyzed by the SAS computer-assisted statistical package for data analysis. This data was analyzed for several different statistical fits. The statistical parameters n, F, α, and r^2 for all the THMFP models are given in Table 36. The n represents the samples used for the model, F is the statistic used for the analysis of variance to determine if the model is adequate. Thus F is calculated by dividing the square of the predicted value of y (in THM or in Cl_2) minus the actual value of y, which

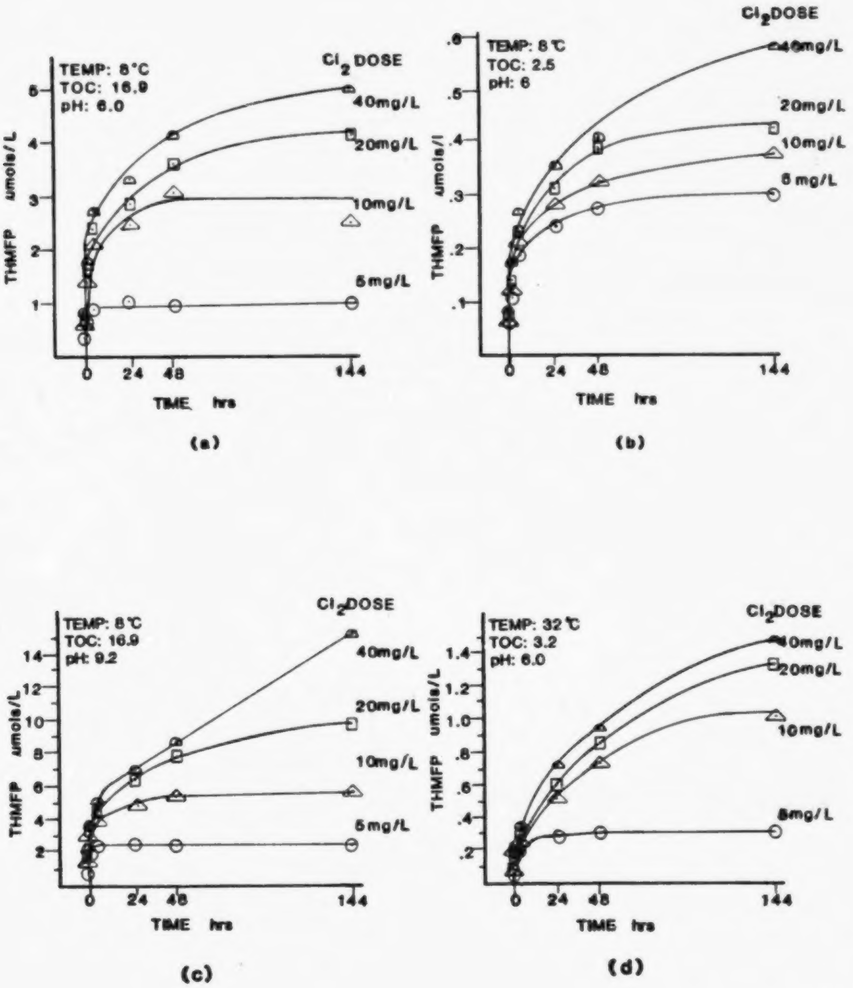


FIGURE 41: THE EFFECT ON THMFP FOR VARYING TOC, pH, TEMPERATURE AND CHLORINE DOSE AS A FUNCTION OF TIME. SAMPLE TIMES WERE AT 0.05 1, 6, 24, 48 AND 144 HOURS

Table 36. Exponents and Statistical Parameters for THMFP Model, $THM = K(Cl)^a(T)^b(TOC)^c(OH)^d(t)^e$

Model No.	Exponents							Statistical Parameters			Conditions
	K	a	b	c	d	e	n	F	α	r^2	
1.	3.73	0.42	0.09	1.08	0.09	0.22	643	1416	10^{-4}	0.92	All data points.
2.	4.84	0.42	0	1.09	0.09	0.22	643	1725	10^{-4}	0.92	All data points.
3.	2.70	0.24	0.17	1.24	0.10	0.26	510	2980	10^{-4}	0.97	Only data points with Cl_2 residual.
4.	4.31	0.25	0	1.24	0.10	0.26	510	3103	10^{-4}	0.96	Only data points with Cl_2 residual.
5.	3.94	0.21	0	1.19	0.10	0.23	183	2160	10^{-4}	0.98	Only data points with Cl_2 residual at 8°C.
6.	3.78	0.20	0	1.23	0.10	0.24	175	1711	10^{-4}	0.98	Only data points with Cl_2 residual at 16°C.
7.	5.47	0.28	0	1.36	0.10	0.31	150	1750	10^{-4}	0.98	Only data points with Cl_2 residual at 32°C.

where: THM = g/l THM $(\frac{1}{127})$ = m/l THM

Cl = Initial chlorine dose in mm/l

TOC = mm/l TOC

OH = mm/l OH

T = °C

t = hours

is the error, into the square of the actual value of y minus the average value of y. Since it is desirable to have a small error, the higher the value of F, the better the adequacy of the model. The alpha, α, value is a fraction of the data that will not be reliably described by the model. The smaller alpha, the more reliable the model. The r^2 term describes what amount of variation of y can be attributed to a linear variation of x as predicted by the model. Perfect correlation, r^2, would be 1.

The parameters for the THM models are shown in Table 36. The relative significance of each one of the variables (TOC, T, t, Cl_2 and pH) can be judged by the exponent. The larger the exponent, the more the variable is significant to THM production. On this basis the order of variable significance for the ranges tested is TOC, followed by Cl_2 dose and time, which are about equal, followed by temperature and then pH. The first model in Table 36 was developed based on all variables and data points, including those where Cl_2 residual had reached zero. The second model excluded temperature and utilized all data. The third and fourth models are identical to (1) and (2) but using only samples that had a Cl_2 residual present. The (3) equation is the most versatile because all variables were significant ($\alpha = 10^{-4}$) and should be utilized by the predictive model. Equations (5), (6) and (7) are developed for the data from the 8°, 16° and 32° data, respectively. In each of the equations the r^2 was slightly improved to 0.98 but the most versatile equation, (3), utilized all variables and had an r^2 of 0.97, was significant to 0.0001 and had less than a 0.01 chance of being inadequate to describe the data. In short, it is a very good model to describe the data. Attempts to incorporate the effect of temperature, using the Arrhenius equation, into the exponent for each parameter were unsuccessful. This can easily be seen by inspecting the exponents in models (5), (6) and (7) as shown in Table 36. The model is given as equation (7) in the text. As shown by the model, TOC has the greatest effect on THMFP followed by time, chlorine dose, pH and temperature.

The statistical analysis from the SAS program appears in the Appendix for the best of the log models, equation 3; only the samples that had a free chlorine residual were used in this analysis. They essentially show that the confidence interval for predicting THMFP from the model is 99.9999% and that 97% of the variation in the observed data is explained by the model. The SAS program printed out both Type I and Type IV analyses for the significance of each variable in the model. However, since the number of observations in each sub-class is unbalanced (for example, 3 pH values and 4 time values), the Type IV analysis is correct. Each independent variable in the model, Cl_2, TOC, temperature, OH^- and time, is shown to be highly significant to THMFP with alpha values of 10^{-4} or less. It is interesting to note that the most and least significant independent variables on THMFP are TOC and temperature, respectively, as shown by the F values in the Type IV analysis. The plot of predicted THMFP versus actual THMFP is shown in Figure 42. The 45° line in the figure graphically demonstrates the model accurately predicts THMFP for the three different waters.

$$\text{THMFP} = 2.70\ (\text{TOC})^{1.24}(\text{Cl})^{0.24}(\text{OH})^{0.10}(\text{T})^{0.17}(\text{t})^{0.26} \qquad (7)$$

This equation can be quite useful for anyone seeking knowledge about THMFP control by design or in a distribution system. For example, Melbourne's chlorine dose ranges from 17 to 28 mg/L, their final pH is approximately 8.0, maximum time in the distribution system is at least 4.0 days and summertime temperatures in the range of 32°C (90°F) are not uncommon. The process control engineer cannot change time, temperature or pH, as that is usually controlled by stabilization requirements. TOC removal can be regulated in the final process by the optimization of coagulation for TOC removal or the addition of other unit processes such as GAC. Plant chlorine dose is controlled by the requirement of a minimum 0.2 mg/L residual at the tap. During the summer, the typical chlorine dose at Melbourne is 28 mg/L. As predicted by equation (7), the final TOC at Melbourne would have to be 2.3 mg/L, approximately 90% removal from the raw water TOC, in order for the THMFP to be less than 0.1 mg/L after 96 hours. This is not possible by coagulation alone for this water, therefore, a disinfectant change or additional unit processes would be warranted.

7.4.4 THMFP Model Summary

A THMFP model was developed from the statistical analysis of over 600 samples for THMFP. These samples were taken from three separate Florida waters and subject to four different chlorine doses, at three different pH's, at three different temperatures for six different times. The model is

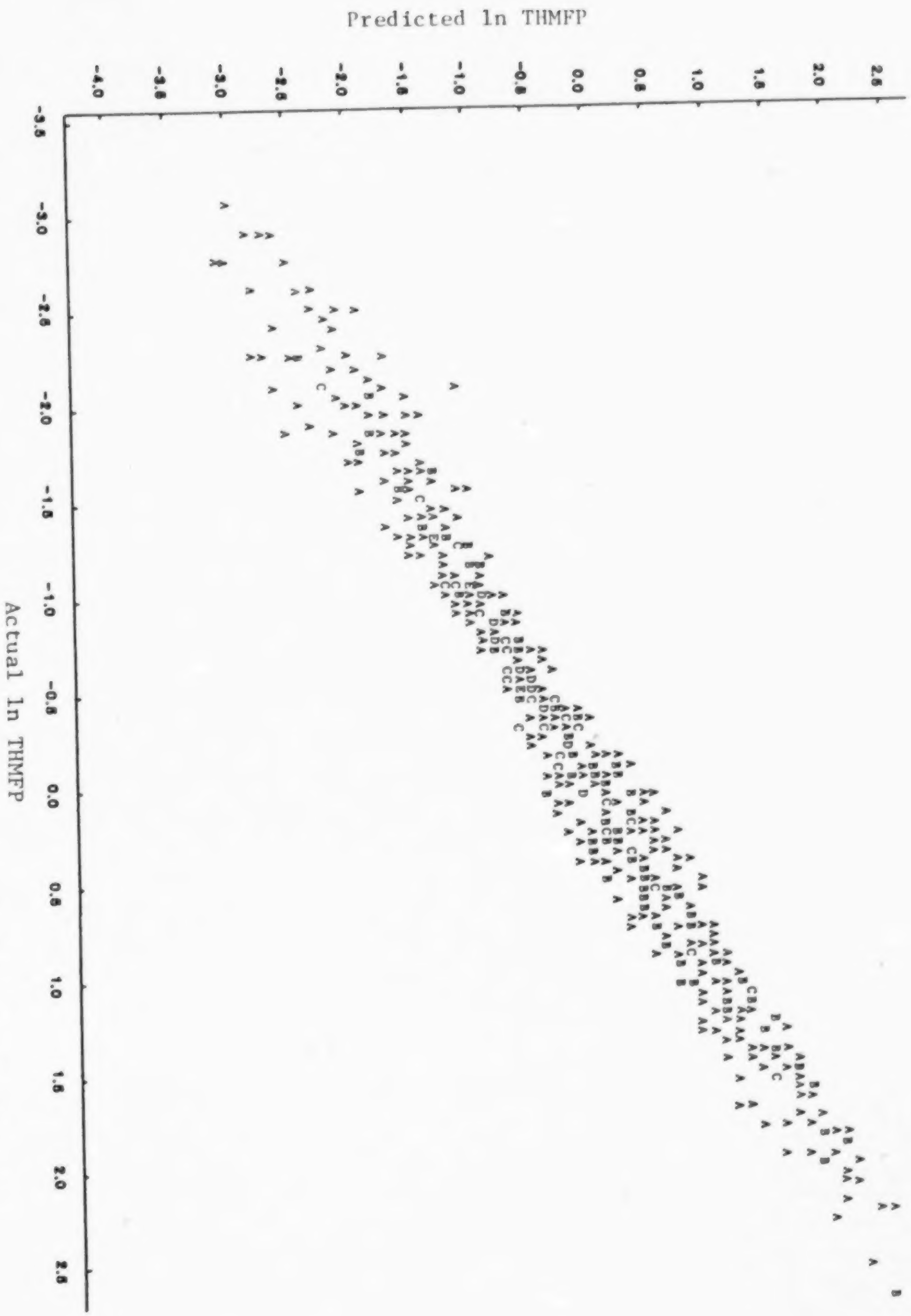


Fig. 42. Predicted ln THMFP versus Actual ln THMFP. A = 1 obs., B = 2 obs., etc.

significant, reliable and could be used as a guide to plant operation or design for THM control.

7.5 Distribution System

In order to accurately assess a treatment process it is necessary to examine the water quality at various points within the distribution system. Figure 43 shows the general location of the sampling points in relation to the Melbourne area. Table 37 gives general information concerning the sampling points including location distance from the water treatment plant and the parameters measured (temperature, chlorine residual, SPC and InstTHM). THM's in this phase are InstTHM's. Figures 44 through 56 give the data concerning temperature (T°), chlorine residual (CR) and specific plate count (SPC) for the 13 sites. Tables A1 through A13 give this data in tabular form. Of the thirteen sites with T°, SPC and chlorine residual data, sites 3, 4, 5, 6, 11, and 12 have data which start during April 1982 and continue to July 1, 1983. Since the water treatment plant underwent various process modifications, the reported sampling period covers all the process modification time periods.

7.5.1 Temperature

Inspection of the sites in increasing distance gives mixed results. Generally in the summer months an increase in distances tends to slightly lower the water temperature due to the insulation properties of subground distribution pipe. Conversely during the winter the water temperature increases again due to the insulation properties of the soil. This cooling and heating effect is more pronounced in this system since the raw water supply is a surface supply and more subject to temperature fluctuations than a ground supply. In any case, the changes with distances are rather insignificant, however seasonal temperatures range from 55°F to 90°F at all sites in the Melbourne distribution system. Temperatures in the Orlando system have a ground water range typically from 45° to 75°.

7.5.2 Chlorine Residual

An inspection of the chlorine residual data showed several significant trends. The first observation was that during the 1982 summer months chlorine residuals were rather low, often close to or zero. An exception to this observation is shown in Figure 48 at site 5 located 15.7 miles from the water treatment plant. This site, while having periods of nearly zero chlorine residual at other times, had residuals in excess of 3.0 mg/L. This site is

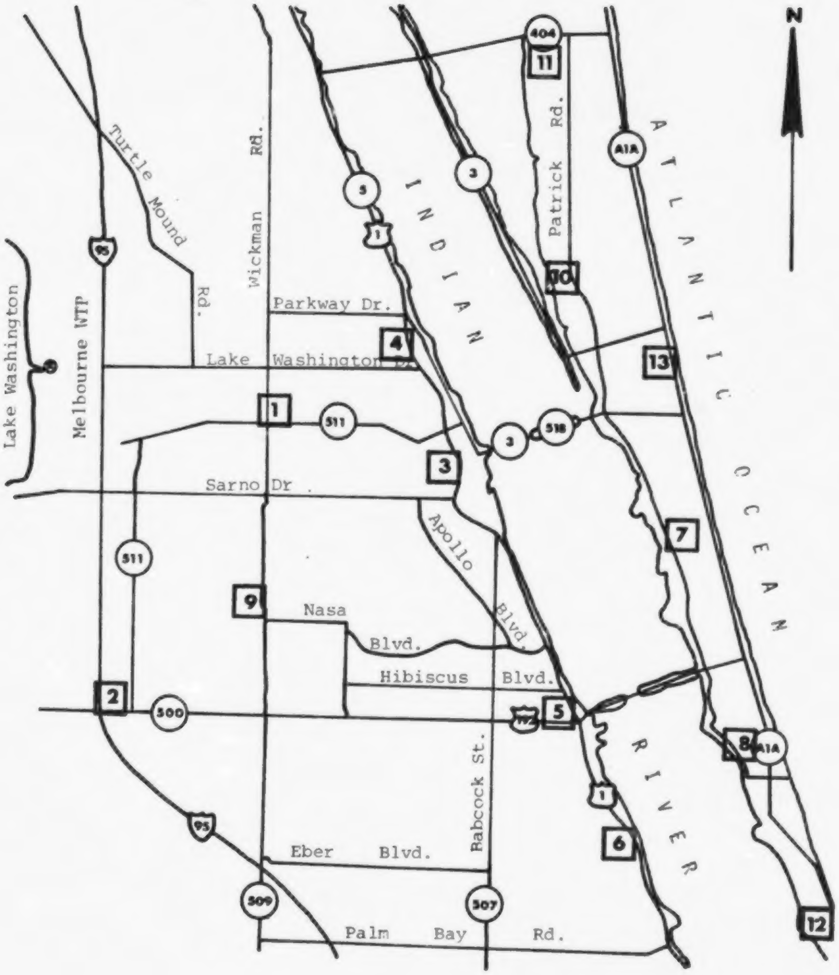

N
404
11
Patrick Rd.
A1A
ATLANTIC OCEAN
3
INDIAN RIVER
5
1
Wickman Rd.
Turtle Mound Rd.
95
Lake Washington
Melbourne WTP
Parkway Dr.
4
Lake Washington Rd.
10
13
1
511
3
518
3
Sarno Dr.
Apollo Blvd.
7
511
9
Nasa Blvd.
Hibiscus Blvd.
2
500
192
5
8
A1A
Babcock St.
1
6
95
Eber Blvd.
509
507
Palm Bay Rd.
12

Figure 43. Sampling Points (denoted in boxes) for the Melbourne Distribution System.

Table 37. Sampling Points Within the Melbourne Distribution System.

Site	Location	Figure	Distance from WTP/ Description	T°	Cl_2 Res	SPC	InstTHM
#1	Wickham Road & Electronics Dr.	(44)	7.6 miles/main line	x	x	x	o
#2	John Rodes Blvd. & Rogers Place	(45)	8.7 miles/main line	x	x	x	o
#3	Pineapple Park	(46)	11.1 miles/close to main line	x	x	x	o
#4	Banberry Lane & Post Road	(47)	11.3 miles/hydrant	x	x	x	x
#5	1400 S. Apollo Boulevard	(48)	15.7 miles/within Bld. hydrant	x	x	x	x
#6	Florida Avenue & Monroe Street	(49)	21.3 miles/main line	x	x	x	x
#7	Coconut Drive & Sea Avenue	(51)	21.7 miles/hydrant	x	x	x	o
#8	Ocean Avenue & Pine Street	(52)	23.3 miles/hydrant	x	x	x	x
#9	Lake Ibis Drive & Ellis Road	(50)	9.6 miles/main line	x	x	x	x
#10	DeSoto Road & S. Patrick Drive	(53)	23.9 miles/hydrant	x	x	x	o
#11	Waterway Drive & S. Patrick Shores	(54)	27.0 miles/hydrant	x	x	x	o
#12	Riverwalk Drive & Seacrest Drive	(55)	29.3 miles/hydrant	x	x	x	x
#13	North A1A & NE Third Street	(56)	28.9 miles/hydrant	x	x	x	x

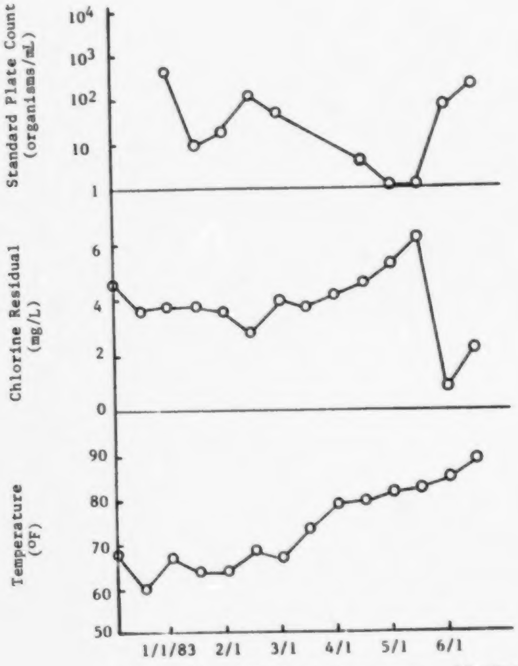


Figure 44. Standard plate count, chlorine residual and temperature at Electronice Drive & Wickham Road, 7.6 miles from the South Melbourne Water Treatment Plant. Site No. 1.

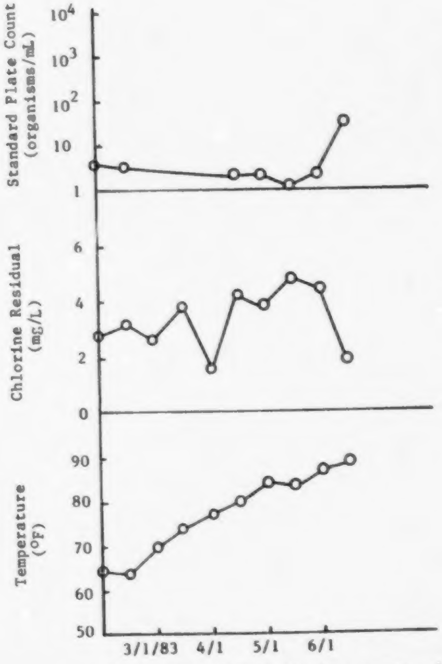


Figure 45. Standard plate count, chlorine residual & temperature at Johns Rodes Blvd. & Rogers Place, NW corner, 8.7 miles from the South Melbourne Water Treatment Plant. Site No. 2.

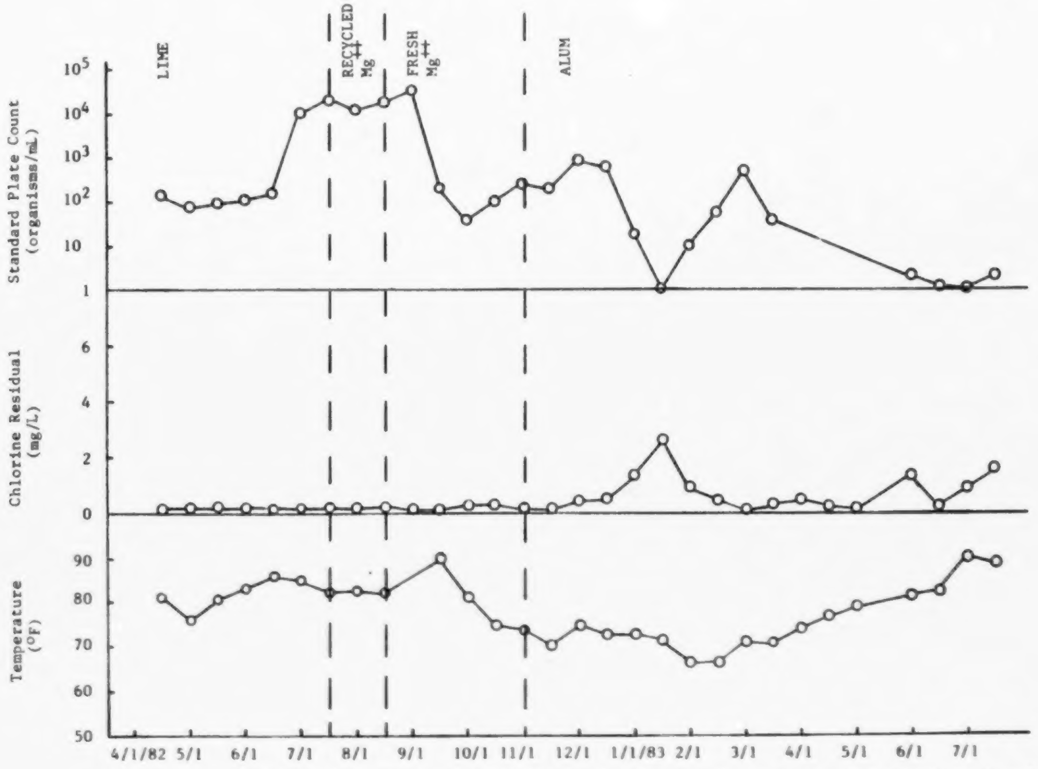


Figure 46. Standard plate count, residual chlorine and temperature at Pineapple Park, 11.1 miles from the South Melbourne Water Treatment Plant. Site No. 3.

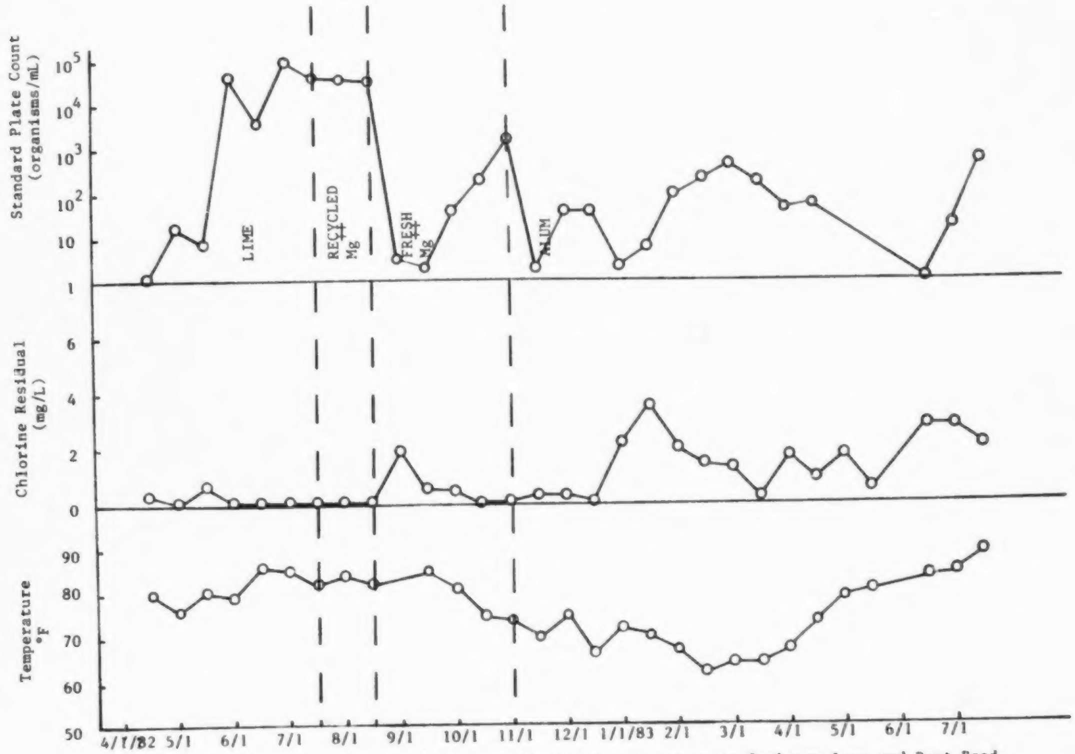


Figure 47. Standard plate count, chlorine residual and temperature at Banberry Lane and Post Road, NW corner, 11.3 miles from the South Melbourne Water Treatment Plant. Site No. 4.

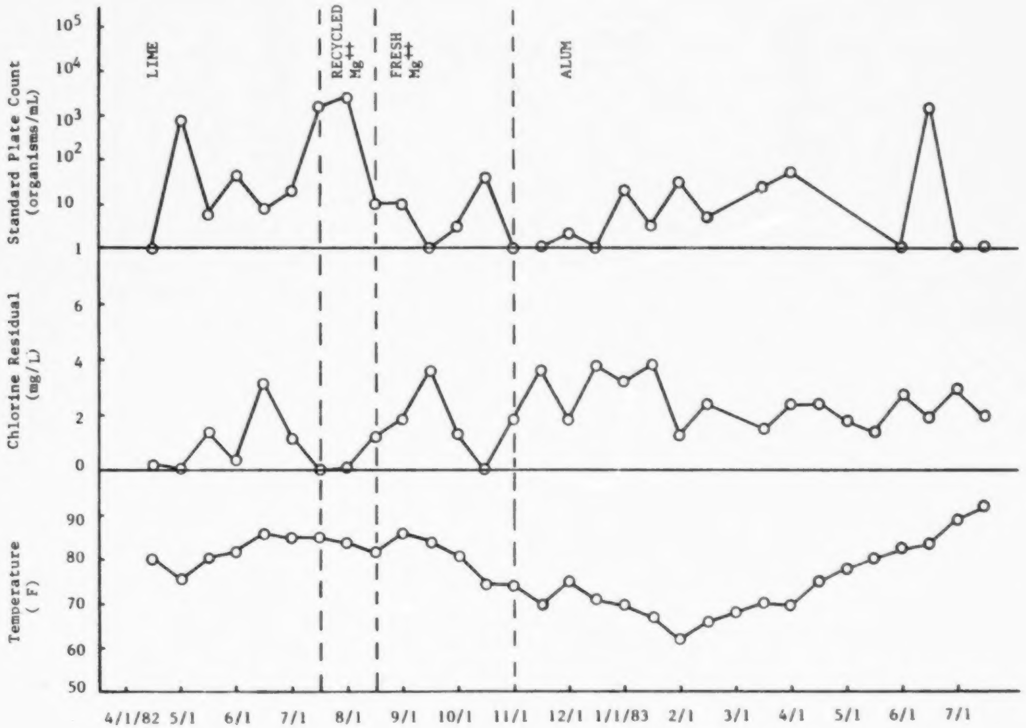


Figure 48. Standard plate count, chlorine residual and temperature at 1400 S. Apollo Blvd., 15.7 miles from the South Melbourne Water Treatment Plant. Site No. 5.

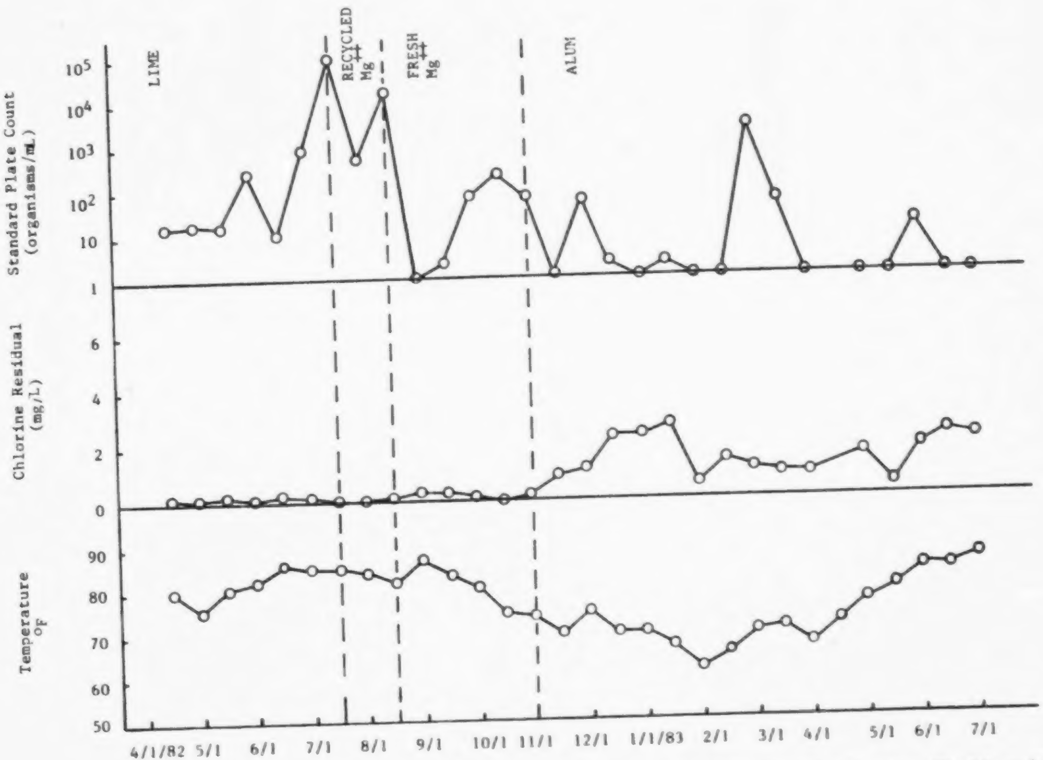


Figure 49. Standard plate count, chlorine residual and temperature at Palm Bay Meter, Florida and Monroe, 21.3 miles from the South Melbourne Water Treatment Plant. Site No. 6.

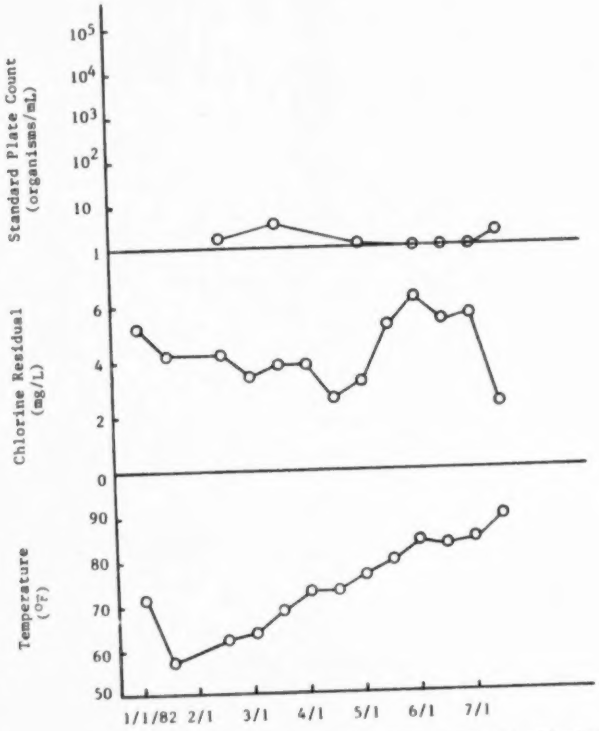


Figure 50. Standard plate count, residual chlorine and temperature at Ellis Road & Lake Ibis Drive, West Melbourne Meter, 9.6 miles from the South Melbourne Water Treatment Plant. Site No. 9.

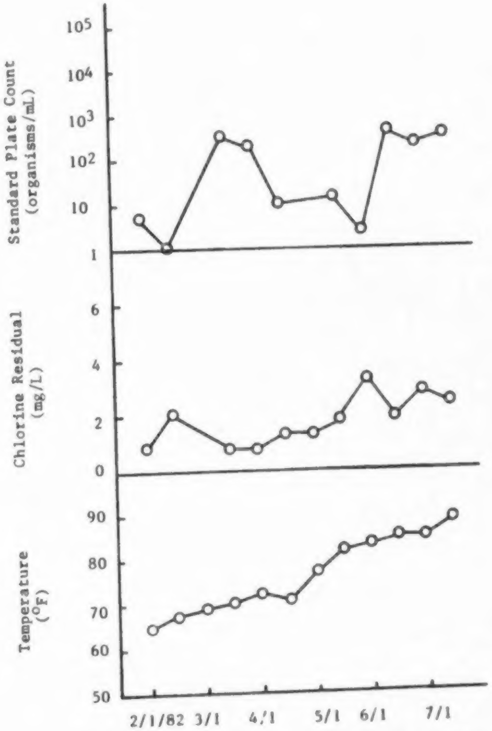


Figure 51. Standard Plate count, Chlorine residual and temperature at Coconut Drive & Sea Avenue, South Side, North Indialantic, 21.7 miles from the South Melbourne Water Treatment Plant. Site No. 7.

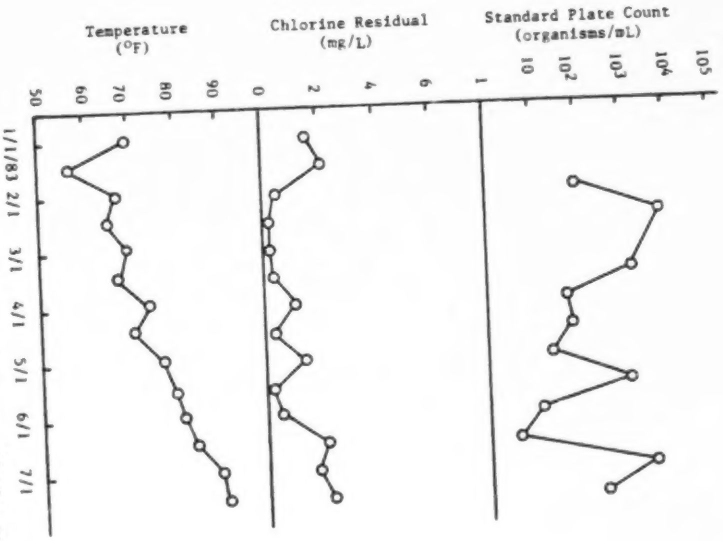


Figure 52. Standard plate count, chlorine residual and temperature at Ocean Avenue & Pine Street, South-West corner, Melbourne Beach City Hall, 23.3 miles from the South Melbourne Water Treatment Plant. Site No. 8

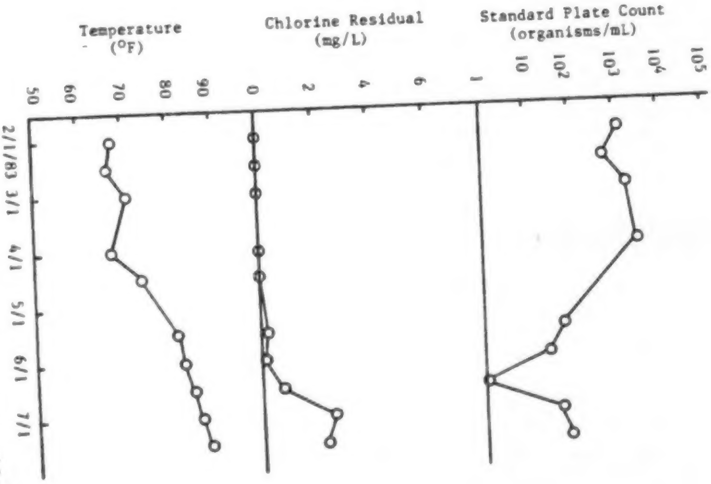


Figure 53. Standard plate count, chlorine residual and temperature at DeSota & S. Patrick Drive, Indian Harbor Beach, 23.9 miles from the South Melbourne Water Treatment Plant. Site No. 10.

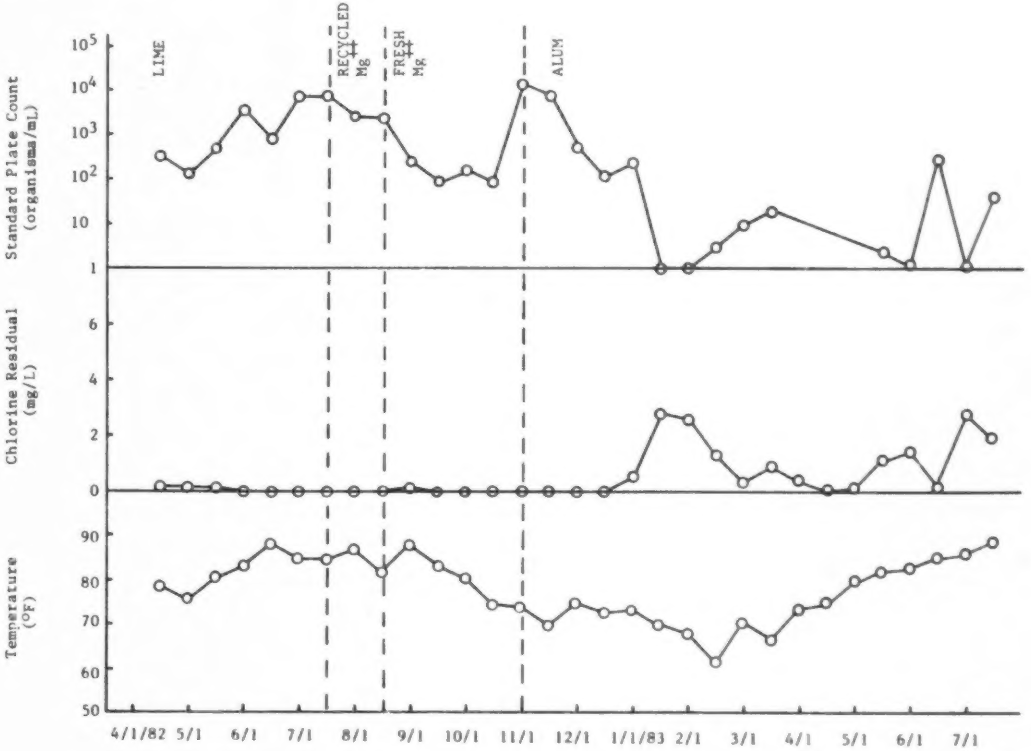


Figure 54. Standard plate count, chlorine residual and temperature at 436 N. Waterway Drive, S. Patrick Shores, 27.0 miles from the South Melbourne Water Treatment Plant. Site No. 11.

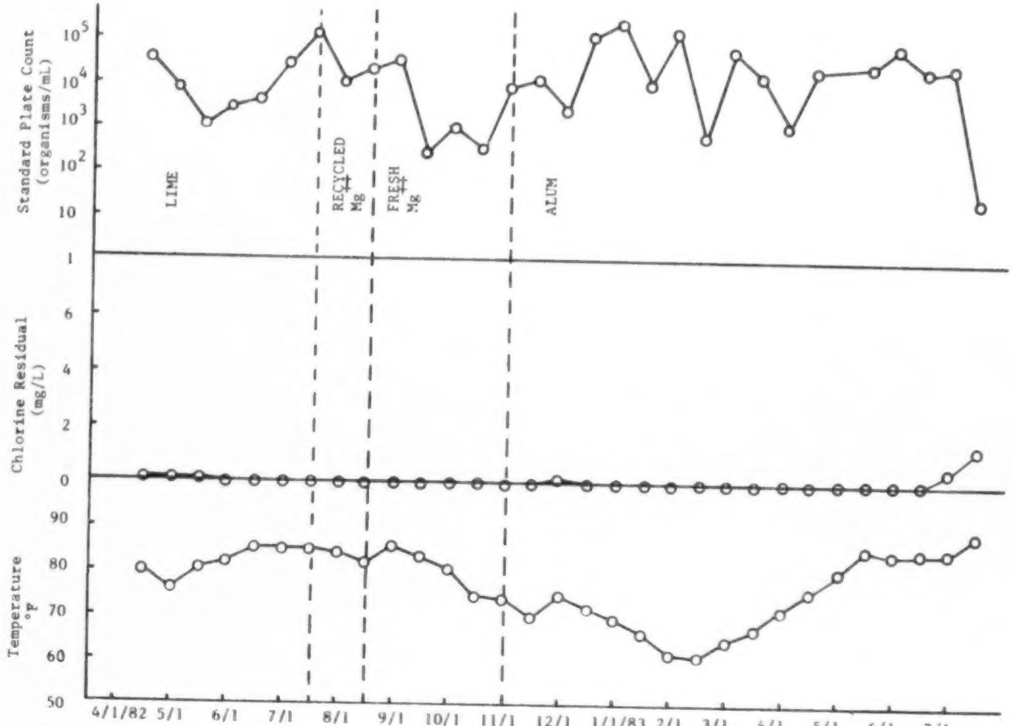


Figure 55 Standard plate count, chlorine residual and temperature at Riverwalk Drive and Seacrest Drive, S.E. Corner, S. Melbourne Beach, 29.3 miles from the South Melbourne Water Treatment Plant. Site No. 12.

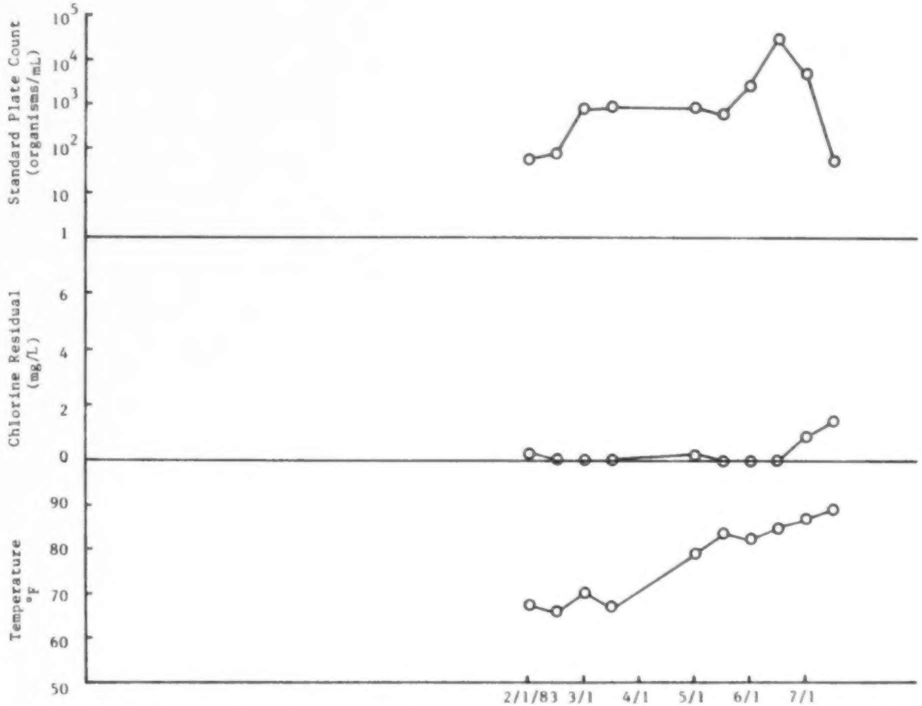


Figure 56. Standard plate count, chlorine residual and temperature at north A1A and Northeast Third Street, 28.9 miles from South Melbourne Water Treatment Plant. Site No. 13.

close to the main line and benefits from a fresh supply. However as shown in Figures 54 and 55 at sites 11 and 12, 27.0 and 29.3 miles away from the plant respectively, a condition of zero chlorine residual is constant throughout the summer months due to the water's high temperature, TOC and distance of travel.

There are several sites such as #3 (Figure 46), 11 (Figure 54), and 12 (Figure 55) in 1982 that showed zero residual regardless of season. This is due in part to the high TOC concentration of the water, but more so to the probable long detention time at these locations. This detention time was estimated as a maximum of three to four days by city personnel, but no exact calculation was made. General statements regarding these residuals are complicated by the intermittent nature of line flushing and increasing chlorine dose at the plant. Melbourne personnel were trying very hard but not succeeding in maintaining a free residual in the distribution system. Site 3 as shown in Figure 46 does show a general increase in residual with a decrease in temperature, specifically note a 2.6 mg/L chlorine residual peak occurs when the water temperature is 73°F, near its 67°F low. This same observation is made at site 11 between December 1982 and February 1983. The real problem is that a chlorine residual could never be maintained in the high TOC concentration Melbourne water during summer conditions.

A second observation is that during the winter months, a more noticeable chlorine residual is apparent throughout the system. Also, during the winter months' lower temperatures the residual does not vary with distance to the degree it does in the summer. A 2.6 mg/L residual is observed at site 3 (Figure 46), 11 miles from plant and at site 11 (Figure 54), 27 miles from plant in January 1983. An exception is found at the most distant site #12 (Figure 55) where no chlorine residual is detected. It would appear, even given the more favorable winter temperatures for chlorine residual, that the long retention time of the Melbourne finished water in the system resulted in complete depletion of chlorine.

The third observation deals with the effects of the various treatment schemes. As previously discussed, the water treatment plant has operated under four coagulation schemes. These schemes in chronological order were: 1) high lime until August 1982, 2) recycled $Mg(HCO_3)_2$ until September 1982, 3) fresh $MgSO_4 \cdot 7H_2O$ until November 1982, and 4) alum from November 1982 to the present. The alum treatment scheme provided the best finished water quality.

The four coagulant schemes, high lime, recycle $Mg(HCO_3)_2$, fresh $MgSO_4$, and alum removed respectively 77%, 74%, 83%, and 93% of the color and 50%, 51%, 53%, and 66% of the TOC. Alum was the best coagulant, removing 10% more color (∿15 cpu) and 13% more TOC (∿4 mg/L) than the second best coagulant fresh $MgSO_4$. The TOC and color removal could have been increased with fresh $MgSO_4$ by increasing pH and dose but serious operational problems would have been experienced due to scaling and sludge handling.

Given a lower color and TOC concentration in the finished water, it would be reasonable to expect a lower chlorine demand and thus a higher residual throughout the system. Inspection of the data in Figure 49 show that a noticeable but varying improvement in chlorine residual is found in the April 1983 data when compared to the April 1982 data a year earlier. This trend holds throughout the entire system with the exception of the most distant points. Thus it may be stated that because of the additional TOC removal the alum treatment scheme has improved the chlorine residual throughout most of the distribution system.

Analysis of the data show that up to 10.0 miles of distance, chlorine residual definitely decreases with distance. However in excess of 10.0 miles the data is more variable with a decreasing trend still evident. Such a response is expected since chlorine residuals decrease with residence and thus contact time. As can be seen, complete depletions of chlorine are regularly experienced within the system at sites 11 and 12 located 27 and 29.3 miles from the plant. These data corresponded to a plant dose of 20 to 30 mg/L chlorine and strongly indicates that chlorine may not be an effective disinfectant for high TOC concentration waters in that a disinfectant residual can not be maintained in the distribution system.

7.5.3 Standard Plate Count

As can be reasonably expected the standard plate count (SPC) should vary somewhat in conjunction with the chlorine residual values. When the chlorine residual is above approximately 0.5 mg/L, the SPC should be generally lower then when the chlorine residual approaches zero. Inspection of the data shows this trend holds true to a general degree. In many cases an increase in chlorine residual prompts a decrease in standard plate count. However this trend is not universal and in a significant number of cases SPC has no quantifiable trend with chlorine residual.

In terms of distance no definite trend of increasing SPC with distance is noticed. A trend is most noticeable in Figure 55 at site 12, the most distant site. The high SPC encountered at this site are probably due to the long residence time which depletes the chlorine residual. On the whole, distance has no single effect.

The maximum SPC shown is 11.1 miles from the plant in August of 1982 with 155,000 org/mL at site 3 in Figure 46 whereas 2,650 org/mL and 10,000 org/mL were observed 27 and 29.3 miles from the plant at sites 11 and 12, respectively. SPCs have been recorded in the Melbourne distribution system as high as 250,000 org/mL but this is attributed to dead ends in the system and may be more related to location with the distribution system than distance.

In terms of treatment schemes the data is complicated by temperature and chlorine residual factors. As stated earlier temperature has an effect on chlorine residual which in turn has an effect on standard plate count. Since the treatment schemes, in some cases, only lasted during a portion of a season, individual comparisons between the treatment schemes is difficult. However it is possible to compare the SPC for the lime-treated water from April 1982 to July 1982 to the alum-treated water from April 1983 to July 1983. Results are mixed but a general decrease in SPC may be seen. This decrease is particularly noticeable in Figures 46, 48, 49 and 54 at sites 3, 5, 6, and 11. Value decreases range up to two orders of magnitude with most decreases around one order of magnitude. The actual range of SPC has decreased from approximately 100-50,000 org/mL to 10-1000 org/mL because of the process change to alum which increased the residual. It should be noticed that this decrease generally was seen for a variety of distances from the water treatment plant.

7.5.4 InstTHM

InstTHM data was collected at six stations for over one year. These six stations include the five sites previously discussed (sites 1, 5, 6, 8, and 9) and one other site. Site 13 is located 28.9 miles from the water treatment plant in Indian Harbour Beach. The InstTHM data for the six sites may be seen in Table 38 along with the water treatment plant finished water InstTHM values. Note that the sites are arranged in increasing linear distance from the plant. The range of InstTHM's varies by coagulant, distance (time), season, and disinfectant ranging from 1299 μg/L to 10 μg/L.

Table 38. InstTHM Data in ug/L for Distribution System.

				Site Number, Linear Distance in Miles					
Disin-fectant	Coagulant	Date	WTP 0	#1 7.6	#9 9.6	#14 15.7	#6 21.3	#8 23.3	#13 28.9
Cl_2	Lime	01/82	477	---	---	---	689	891	886
Cl_2	Lime	02/82	351	617	572	765	613	843	881
Cl_2	Lime	02/82	307	503	513	811	654	898	774
Cl_2	Lime	04/82	335	518	409	726	609	681	537
Cl_2	Lime	05/82	411	704	694	872	720	887	---
Cl_2	Lime	06/82	379	1063	---	1232	947	1299	1284
Cl_2	Recycle	07/82	---	---	---	---	---	---	---
Cl_2	Recycle	08/82	---	---	---	---	---	---	---
Cl_2	$MgSO_4$	09/82	514	638	347	1038	660	931	887
Cl_2	$MgSO_4$	10/82	227	---	461	681	570	621	705
Cl_2	$MgSO_4$	11/82	214	441	320	578	436	---	608
Cl_2	Alum	12/82	208	---	677	590	377	737	553
Cl_2	Alum	01/83	---	---	---	---	---	---	---
Cl_2	Alum	02/83	217	364	259	---	---	---	558
Cl_2	Alum	03/83	263	422	372	574	449	446	549
Cl_2	Alum	04/83	209	---	373	401	393	497	475
Cl_2	Alum	05/83	241	---	335	---	485	427	465
Cl_2	Alum	06/83	262	---	388	---	479	431	678
NH_2Cl	Alum	07/83	10	---	8	---	---	---	33
NH_2Cl	Alum	08/83	30	---	30	33	---	25	---

Inspection of the data shows a definite trend of increasing InstTHM's with increasing distance. This trend holds true through all seasons with the trend more pronounced in the warmer months. The maximum values are generally approached when the distance exceeds 10 miles. In some cases the increases in InstTHM's can be four-fold in comparison with the water treatment plant finished water values. This trend of increasing InstTHM's would hold as long as a chlorine residual was present.

The increase in InstTHM values during the warmer months corresponds with the temperature and standard plate count increases and chlorine residual decreases noticed during warmer periods. Given the relationships stated earlier for THMFP this situation is not unexpected.

When comparing the InstTHM data with treatment schemes, the effect of distance, temperature, chlorine residual, and standard plate counts tend to obscure any trends. However a comparison of April 1982 and April 1983 data show that the switch from lime to alum has definitely decreased the concentration of THMFP in the finished water and the distribution system to less than 50 μg/L. The dramatic decreases in July and August 1983 are discussed in a later section. Inspection of the available data leads to several qualitative trends:

1. Chlorine residual in the distribution system was dependent on at least three factors, (A) the distance from the water treatment plant, (B) the plant process, and (C) the water temperature.
2. Chlorine residual corresponded to temperature with low residuals during the warmer months and higher levels during the colder months.
3. Chlorine residual decreases with distance from the water treatment plant because of increased contact times.
4. Chlorine residuals slightly increased with the use of alum in the treatment scheme.
5. Standard plate counts do not show any strong, definite trends but are generally directly proportional with chlorine residual values.
6. InstTHM's show a definite trend of increasing concentrations with increasing distance.
7. InstTHM's exhibit a definite increase during warmer months which corresponds to a low or zero chlorine residual.

8. The use of alum has shown a tendency to decrease THMFP concentrations when compared to the use of lime.

7.5.5 Chlorine Residuals

Beginning in July 1983, the use of chloramines as disinfectant was initiated replacing the use of chlorine. While the data are very limited, some facts are apparent. Inspection of the data shows that since the introduction of chloramines the chlorine residuals have shown slight declines. Such declines are to be expected during the warmer months. However, in general, the chlorine residual is higher during the period of July and August 1983 than during the same period, a year earlier. Thus it would appear in this short term period, that the use of chloramines promotes a higher residual value because of a slower reaction rate of chloramine. This trend is evident in Figures 46, 47, 54 and 55 at sites 3, 4, 11, and particularly at 12 where the first non-zero chlorine residual in history was recorded in July 1983, 0.5 mg/L.

In terms of distance no significant trend is apparent except at site 12. Throughout the period of record this site has exhibited chlorine residuals near zero. With the introduction of chloramines a residual is now being detected up to 1.4 mg/L. Thus in the furthermost reaches of the distribution system, chloramines are having an immediate impact.

7.5.6 Distribution System Summary

The analysis of the standard plate counts show a strong correlation with chlorine residual during the two-month period of July-August 1983. As chlorine residuals increase, the plate counts decrease and vice versa. While the data is slightly obscured by the use of a different treatment scheme (lime) during the previous year, current standard plate counts (1983) are less than experienced in 1982. The SPCs are in excess of 10,000 org/mL at the closest and furthest sites during July/August of 1982. The SPC were reduced to less than 1000 org/mL and at both sites minimums of 90% reduction were found. In terms of distance, no definite trends are noted except for site 12 where the lowest SPC ever recorded has been obtained during the use of chloramines.

Changing to chloramines has significantly reduced InstTHM's. Data for July and August 1983 show that dramatic decreases in InstTHM's have been recorded for both the finished water and in the distribution system. In all cases the reduction in concentration was greater than one order of magnitude. For example, from June to July drops of 262 μg/L to 10 μg/L, 388 μg/L to 8 μg/L and 678 μg/L to 33 μg/L were experienced. While the concentrations tend to rise with distance, the absolute increase is very small compared with earlier chlorine-disinfectant results as shown by the reduction in maximum InstTHM's from 678 μg/L to 33 μg/L at Site 13.

While the data base for chloramines is rather small, indications exist at this time favoring the use of chloramines. These trends are a higher chlorine residual, lowered standard plate counts and a dramatic decrease in InstTHM which has drastically improved water quality. This data will continue to be gathered by Melbourne and hopefully published in the open literature.

The purpose of the distribution system phase was to demonstrate the improvement in water quality in the Melbourne distribution system after the installation of chloramine disinfection in July 1983. The original plan was to identify several sampling points within the distribution including the plant and to report residual, standard plant count, trihalomethanes and temperature. Melbourne had initiated a sampling program one year earlier to document the water quality in the system.

The city personnel sampled regularly for THM's before the initiation of the distribution system phase of the project, however the location of the sampling points varied because of access and preference. These initial sites were 6, 8, 9, 11, 12, and 13. Some of these points were located in buildings at taps on sinks and were subject to irregular use which led to poor water quality. In March 1983, the city personnel installed taps into fire hydrants or into the main line located at these sites and the others shown in Table 38 in order to obtain a more realistic status of water quality in the distribution system. The sites the city presently uses for THM sampling are 4, 5, 6, 9, 12, and 13. Some THM samples were also taken from sites 2 and 10. All of the THM data is InstTHM and is given in the Appendix in Tables A1 through A13. All site locations where samples were taken for THM analysis in the distribution phase are denoted in Table 38.

The sampling points given in Table 38 represent sites near, midway, or at the extremities of the distribution system. There were no booster stations utilized at Melbourne for chlorine addition during the collection of this data. The chlorine was only added at the plant in very high doses, 20-30 mg/L, during the sampling period with the exception of the change to chloramines in July 1983. The typical ammonia dose now is 1-2 mg/L which is preceded by 5-8 mg/L chlorine. Originally the ammonia was added before the chlorine to reduce THMFP but the order was switched due to high color complaints. There have been no recent color complaints although raw color is around 200 cpu, and the InstTHM is still less than 50 µg/L although it has increased from the 10-15 µg/L from the first sequence of chemical addition.

These data are not as complete as hoped because of construction delays implementing the chloramine system but they do indicate a significant improvement in water quality at the tap with respect to SPC, InstTHM, and chlorine residual. It will be very interesting to observe consumption and complaints of Melbourne water in the next few years especially at the extremities of the distribution system where the quality was the worst.

7.6 Alternate Disinfectant Phase

The objective of this phase was to evaluate disinfectants other than chlorine and to compare their performance to that of free chlorine. Free chlorine, in addition to serving as the primary disinfectant at the Melbourne Water Treatment Plant, is also utilized to maintain a disinfectant residual in the distribution system, and to oxidize organic color. However, the use of free chlorine as primary disinfectant has resulted in high concentrations of trihalomethanes being formed. Therefore, alternate disinfectants were evaluated for THM formation as well as color removal and residual maintenance.

Figure 57 gives a general overview of the experimental sequence used. All water used in these experiments was taken from a point in the Melbourne water treatment plant after filtration and prior to chlorination. Water taken from this point is referred to in this section as finished water. In the first experiments each single disinfectant was tested for its ability to remove color from Melbourne's finished water. From this data, the dose required to meet the maximum drinking water color standard (i.e., 15 cpu) was determined for each disinfectant.

The second series of experiments were to determine the rate at which disinfectants dissipate under the conditions anticipated at the Melbourne Water Treatment Plant as well as in the distribution system. These experiments involved varying the doses of the various disinfectants, and monitoring the residual over time at various temperatures. The effect of temperature on

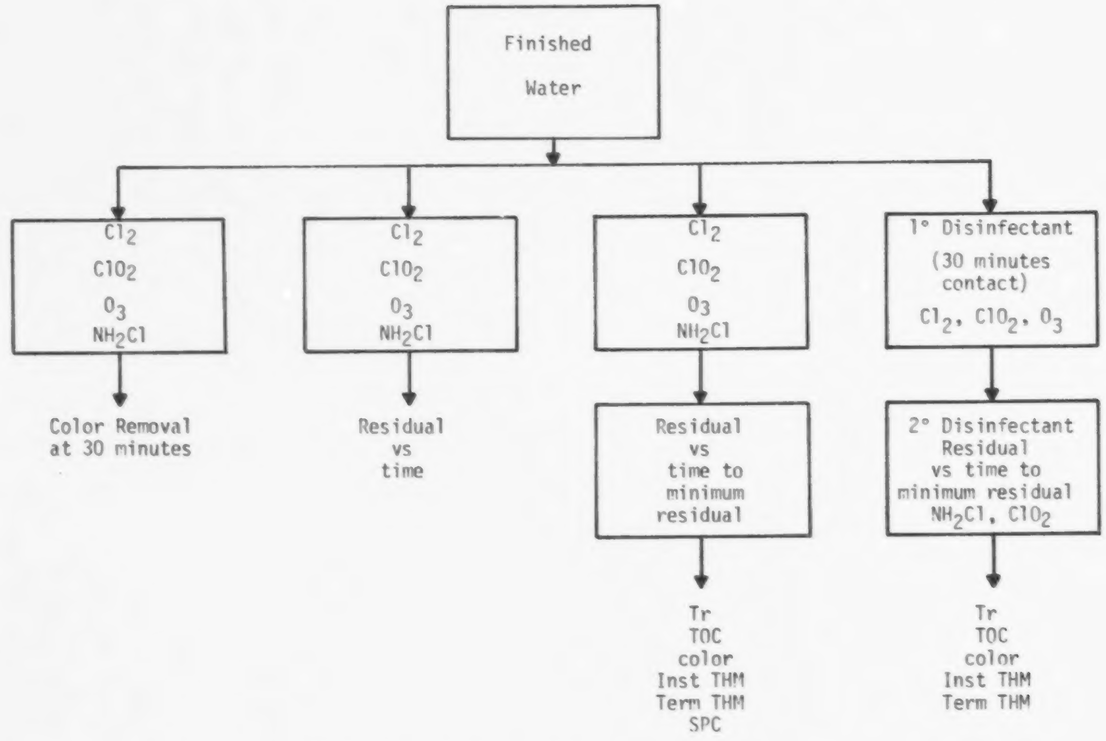

Finished Water
Cl_2
ClO_2
O_3
NH_2Cl
Color Removal at 30 minutes
Cl_2
ClO_2
O_3
NH_2Cl
Residual vs time
Cl_2
ClO_2
O_3
NH_2Cl
Residual vs time to minimum residual
Tr
TOC
color
Inst THM
Term THM
SPC
1° Disinfectant
(30 minutes contact)
Cl_2, ClO_2, O_3
2° Disinfectant Residual vs time to minimum residual NH_2Cl, ClO_2
Tr
TOC
color
Inst THM
Term THM

Figure 57. Flow Chart for the Alternate Disinfectant Phase

dissipation rate is particularly important at Melbourne since the water source is a surface water body, Lake Washington. Seasonal temperature fluctuations therefore exert as great an influence on disinfectant demand as does water quality.

The third series of experiments investigated the water quality resulting from the treatment of Melbourne's finished water with the various disinfectants tested. The parameters monitored included the final concentrations of TOC, InstTHM, TermTHM and color corresponding to a minimum residual. The time to reach a minimum disinfectant residual (0.6 mg/L for monochloramine and 0.5 mg/L for other disinfectants) was also measured.

In the final series of experiments, the effect of four different pairs of the disinfectants on finished water quality was tested. A primary disinfectant was applied followed in thirty minutes by a secondary disinfectant. When the total residual reached the minimum concentrations described above for single disinfectants, the various water quality parameters were measured.

7.6.1 Color Removal by Single Disinfectants

Chemical disinfectants, in addition to providing bacteriological protection, are often used for the removal of color in water supplies. At Melbourne, in order to produce a final product that is aesthetically acceptable, the color must be reduced to concentrations lower than those obtained by coagulation and filtration alone. In the past, breakpoint chlorination has accomplished this color reduction. However, the resulting InstTHM concentrations, an unavoidable consequence of chlorine usage, were unacceptably high. In evaluating disinfectants other than free chlorine for use at Melbourne, their ability to reduce color concentrations is an important consideration. In these experiments, finished water from the Melbourne Water Treatment Plant was treated with varying doses of each disinfectant. After a thirty-minute reaction period, the resulting color was measured and the relative abilities of each disinfectant compared.

Color reduction using free chlorine is demonstrated by the data in Figure 58 and Table 39. In these tests, temperature exerted little, if any, influence on color reduction. Figure 58 shows that color reduction was directly proportional to chlorine dose in the range of 0-10 mg/L. By extrapolation from this figure, approximately 20 mg/L chlorine would be required to reduce color to 5 cpu within the thirty-minute contact period for the

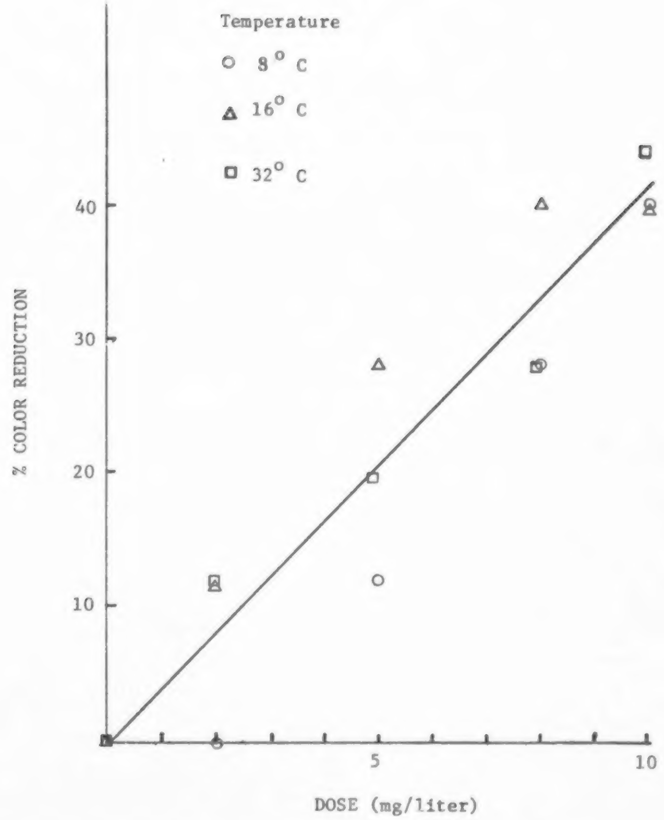


Figure 58 Color reduction by free chlorine at three temperatures. Initial color = 25 cpu. Reaction time = 30 minutes.

Table 39. Color Reduction by Free Chlorine.
Reaction Time = 30 minutes.

Color (cpu)

Dose mg/L	Temperature (°C) 8°	16°	32°
0	25	25	25
2	25	22	22
5	22	18	20
8	18	15	18
10	15	15	14

magnesium coagulated water. Data in Table 40 indicate that longer contact periods can also reduce color to 5 cpu. While chlorine is effective in reducing color, THM concentrations resulting from the use of chlorine can be as high as 500 mg/L. Reducing color to 15 cpu requires a much lower chlorine dose. Data from Tables 39 and 40 indicate a color level of 15 cpu can be reached with as little as 2 mg/L chlorine.

Color reduction using monochloramine is shown in Figure 59 and Table 41. These data suggest that percentage of removal is proportional to the logarithm of the chloramine dose. If the pattern is extrapolated to include a finished color of 5 cpu (80% removal), the chloramine dose required is impracticably high. The data do show that percentage of color reduction is temperature dependent when chloramines are used. No appreciable color removal was noted for any dose or temperature. It appears that chloramines are inefficient, at best, for color removal.

Color reduction by ozone is shown in Figure 60 and Table 42. Increasing the ozone dose increased color removal at all temperatures. Color reduction to less than 5 cpu (>80% reduction) was possible at all temperatures when sufficiently high doses were applied. Figure 60 shows that between 15 and 20 mg/L applied ozone was required to reduce color to less than 5 cpu and about 4-6 mg/L was required to reduce color to 15 cpu. These data indicate that percentage of color reduction may be limited to about 80-90%. There was no clear difference in color reduction at the different temperatures tested. In separate experiments, color reduction by ozone was shown to be practically instantaneous on application.

Color reduction by ClO_2 is described in Figure 61 and Table 43. Figure 61 shows that percentage of color reduction was nearly linear at all temperatures up to 5 to 10 mg/L. The dose required to reach 5 cpu in the finished water was approximately 6-9 mg/L for a thirty-minute contact period. Doses higher than 10 mg/L had little effect on color reduction. This may be caused by the color of unreacted ClO_2, which has a yellow-green hue. A final color of 15 cpu was reached with doses as low as 2-4 mg/L. Color reduction was greater at higher temperatures with the best color removal occurring at ambient temperature of 22°C. The use of ClO_2 in doses greater than 2 mg/L is currently not allowed in Florida by FDER.

Table 40. Residual Color vs. Time and Chlorine Dose at 22°C.

Cl Dose (mg/L)	Color (cpu)						
	Time (min.)						
	1	3	5	10	30	60	120
0	25						
2	22	22	20	18	18	18	15
5	15	15	15	15	15	15	15
5(dup)	15	15	15	12	12	12	12
10	15	15	12	12	9	8	9
20	12	11	9	9	9	8	5
30	10	10	5	5	5	5	5

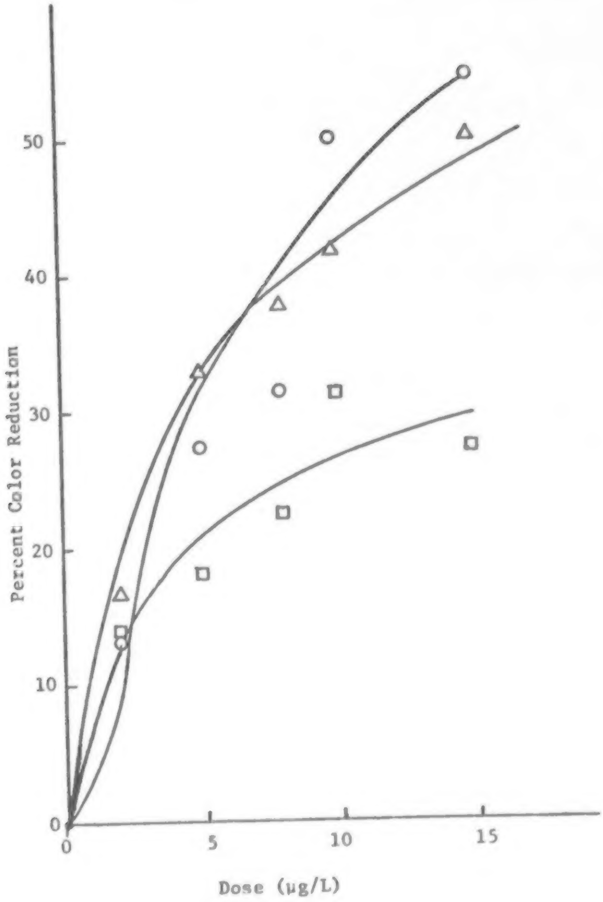


Figure 59 Color removal vs monochloramine dose in finished Melbourne water at 8°C (□); 16°C (○); and 32°C (△). Initial color was 22-24 cpu. Reaction time = 30 minutes.

Table 41. Color Reduction by Monochloramine.
Reaction Time = 30 minutes

Temp. °C	Dose (mg/L)	Initial Color (cpu)	Final Color (cpu)
8	2	22	19
	5		18
	8		17
	10		15
	15		16
16	2	22	19
	5		16
	8		15
	10		11
	15		10
32	2	24	20
	5		16
	8		15
	10		14
	15		12

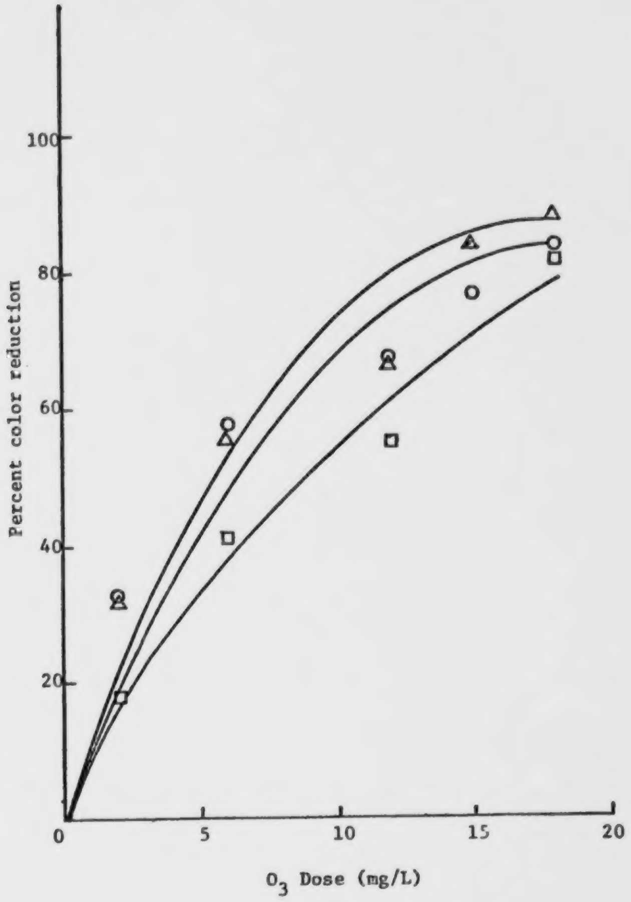


Figure 60 Color reduction by ozone at 8°C (□), 16°C (○), and 32°C (△). Initial color 22-25 cpu. Reaction time = 30 minutes.

Table 42. Color Reduction by Ozone.
Reaction Time = 30 minutes

	Color (cpu)		
	Temperature (°C)		
O_3 Dose (mg/L)	8°	22°	32°
0	22	24	25
2	18	16	17
6	13	10	11
12	10	8	8
15	--	6	4
18	4	4	3

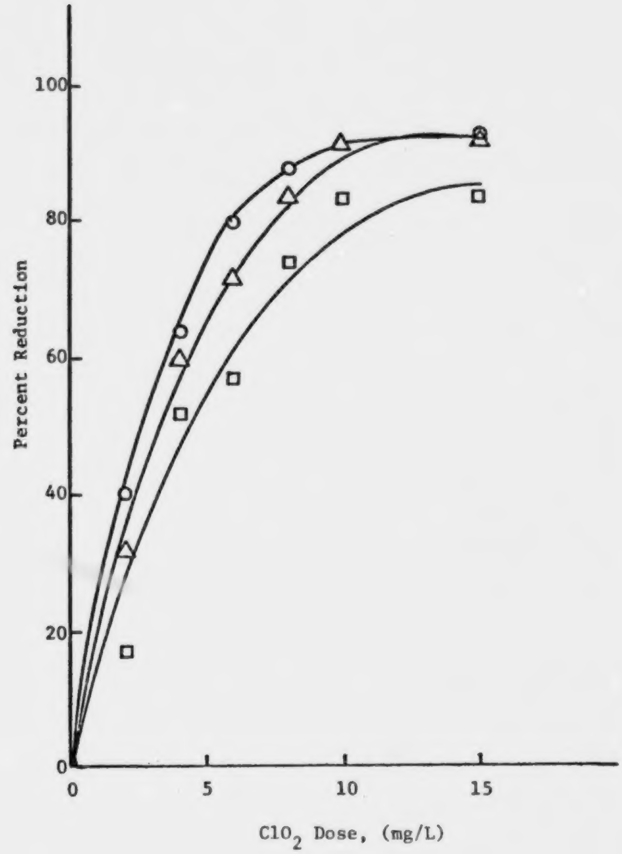


Figure 61 Color reduction by ClO_2 at 8°C (□); 16°C (○); and 32°C (△). Initial color 23-25 cpu. Reaction time = 30 minutes.

Table 43. Color Reduction by ClO_2
Reaction Time = 30 minutes

	Color (cpu)		
	Temperature (°C)		
ClO_2 Dose (mg/L)	8°	22°	32°
0	23	25	25
2	19	15	17
4	11	9	10
6	10	5	7
8	6	3	4
10	4	2	2
15	4	2	2

Of the alternate disinfectants tested, only ClO_2 and O_3 were capable of reducing color to 5 cpu or less and then only at high doses. Overall performance of these disinfectants for color removal in a thirty-minute reaction period can be ranked from these results as follows: ($ClO_2 > O_3 > Cl_2 >> NH_2Cl$. For all of the disinfectants tested, attempts to reduce color to less than 5 cpu in thirty minutes requires excessively high disinfectant doses ($NH_2CL \sim 100$-5000 mg/L; $Cl_2 \sim 20$ mg/L; $O_3 \sim 15$-20 mg/L and $ClO_2 \sim 6$-9 mg/L). From these results it appears that color reduction would be best accomplished by means other than disinfectant addition.

7.6.2 Single Disinfectant Dissipation Rates

In these experiments, each disinfectant was evaluated for its ability to maintain a minimum residual concentration in finished Melbourne Water. One liter samples of water were treated with varying doses of each disinfectant (Cl_2, 5, 10, 20, and 40 mg/L; NH_2Cl 3, 6, 12, and 25 mg/L; O_3 0.5, 2.0, and 10.0 mg/L; and ClO_2 0.5, 2.0, and 10.0 mg/L). The residual in each sample was then monitored over time until it had reached a specified minimum concentration (0.6 mg/L for NH_2Cl and 0.5 mg/L for all others) or for six days whichever came first (i.e., the maximum detention time for the distribution system).

Data for chlorine dissipation are presented in Table 44, and Figures 62, 63, and 64. Initial chlorine utilization was quite rapid at all temperatures, ranging from 7.4 mg/L-hr for the 10 mg/L dose at 8°C to 16.2 mg/L-hr for the 40 mg/L dose at 32°C. After the first hour, dissipation more nearly approximated a first order decay reaction. These data show that at 8°C a 20 mg/L chlorine dose was sufficient to maintain a minimum residual of 0.5 mg/L for at least six days. At higher temperatures, however, higher chlorine doses were required. At 32°C, a dose greater than 20 mg/L was required to maintain a residual for the full six day period. Initial chlorine demand also increased with temperature. Interpolating from Figure 63, 0.5 mg/L residual was probably reached at about four days with a 20 mg/L initial chlorine dose. At 32°, all doses were exhausted before six days. The 20 mg/L dose reached zero residual within 24 hours and the 40 mg/L dose probably reached zero at about four days.

Table 45 shows chlorine dioxide residuals versus time for 8°, 16°, and 32°C. ClO_2 dissipated much more rapidly than chlorine. As with chlorine,

Table 44. Chlorine Residual vs Time.

Dose (mg/L)	time (hrs)	Chlorine Residual mg/L Cl Temperature °C 8	 16	 32
5	1	0	0	0
	6	0	0	0
	24	0	0	0
	48	0	0	0
	144	0	0	0
10	1	2.6	0.7	0
	6	1.0	0	0
	24	0	0	0
	48	0	0	0
	144	0	0	0
20	1	10.3	7.9	6.2
	6	9.0	5.4	1.8
	24	6.2	2.9	0
	48	4.5	1.0	0
	144	1.3	0	0
40	1	28.7	26.2	23.8
	6	26.1	21.5	15.6
	24	23.5	18.3	8.4
	48	20.4	15.0	4.4
	144	14.6	9.5	0

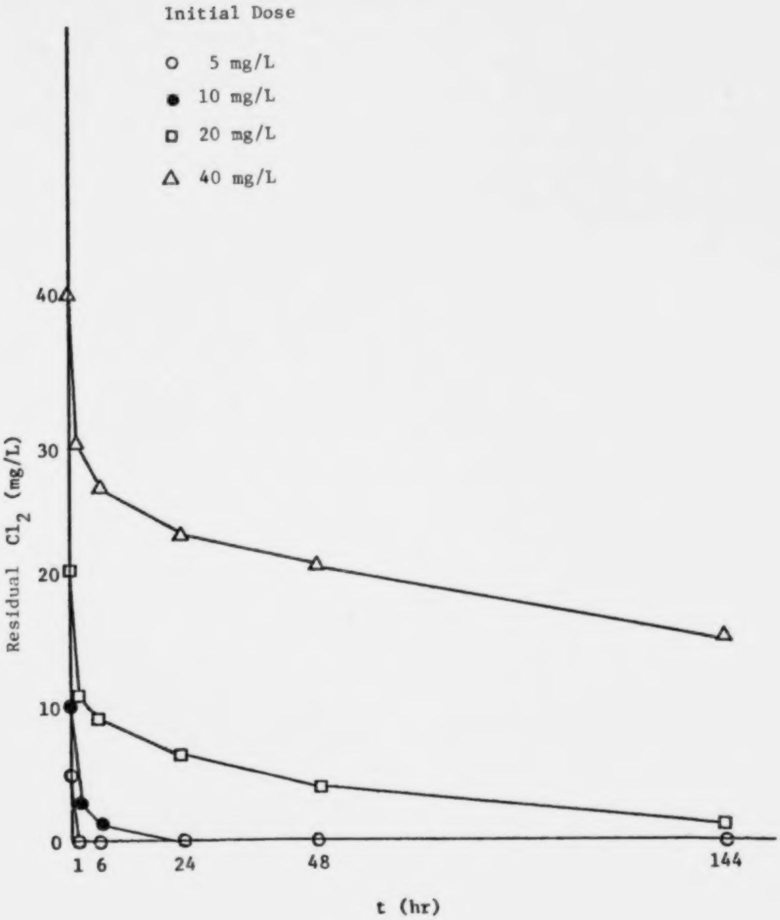


Figure 62 Chlorine residual vs time at 8°C.

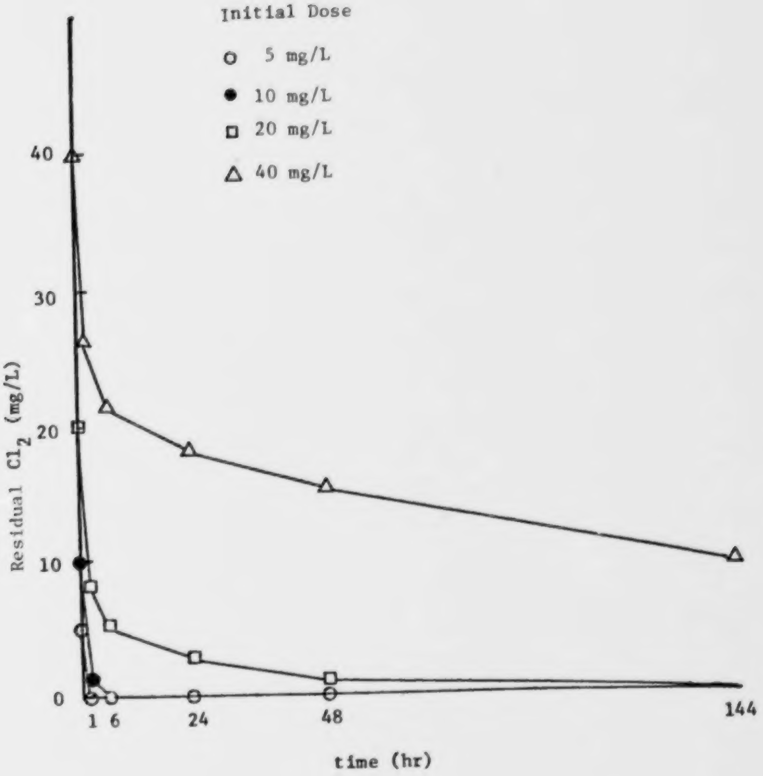


Figure 63 Chlorine residual vs time at 16°C.

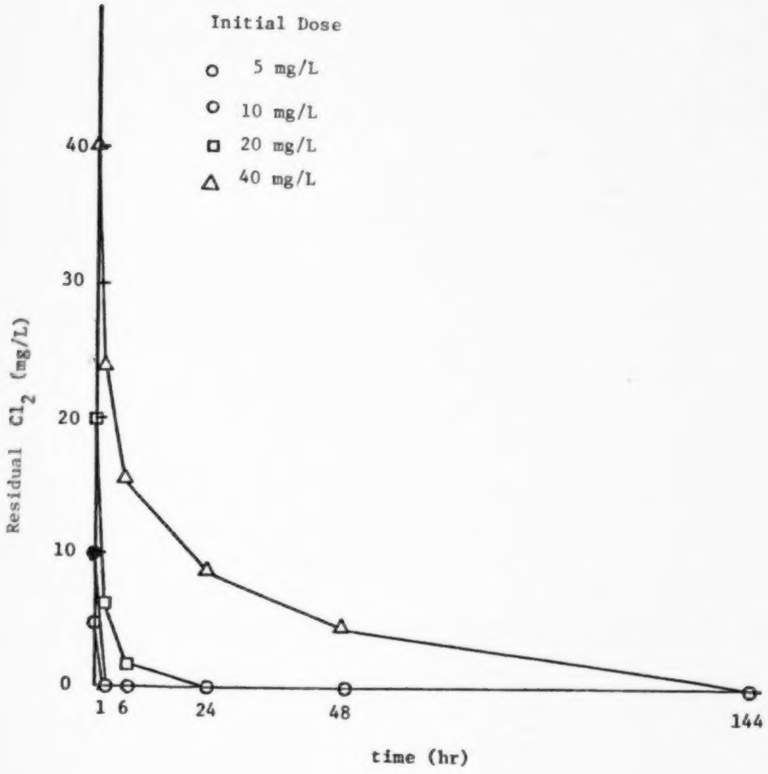


Figure 64 Chlorine residual vs time at 32°C.

Table 45. Chlorine Dioxide Residual vs Time.

Initial Dose (mg/L)	time (days)	ClO_2 Residual (mg/L) as ClO_2)		
		Temperature °C		
		8°	16°	32°
0.5	0	0.5	0.5	0.5
	1	0.3	0.25	0.2
	3	--	--	--
	4	--	--	--
2.0	0	2.0	2.0	2.0
	1	0.8	0.8	0.8
	2	0.4	0.5	0.3
	3	--	--	--
	4	--	--	--
10.0	0	10	10	10
	1	3.2	2.5	2.0
	2	1.5	1.5	1.3
	3	0.9	0.8	1.2
	4	0.5	0.4	0.6

initial demand was high with as much as 80% being consumed in the first 24 hours. Subsequent dissipation more closely followed a first order decay model with a decay constant of approximately 0.7 day^{-1}. Figures 65, 66, and 67 show little difference in dissipation rate between the temperatures tested. It is also evident from these figures that an initial dose considerably higher than 10 mg/L would be required to maintain a residual for six days. Such high doses would not be compatible with potable water treatment due to the potential formation of high concentrations of chlorite ions. Chlorine dioxide persisted longer than equal doses of chlorine. Whereas 5 mg/L doses of chlorine were completely consumed within 24 hours, 0.5 mg/L doses of ClO_2 had a measurable residual after 24 hours.

Data for chloramine dissipation over time are given in Table 46 as well as in Figures 68, 69, and 70. At 8° and 16° chloramine dissipation occurs at a steady rate of 0.3 to 2 mg/L-day depending on the initial concentration. No significant difference was found between dissipation at 8° and 16°. Figure 69 shows that for lower doses and higher temperatures chloramine dissipation follows a pattern similar to first order decay.

A minimum residual of 0.6 mg/L as Cl was maintained for all doses tested at 8° and 16° for at least seven days. At 32°, a 3 mg/L chloramine dose decays to less than 0.6 mg/L within three days. A dose of 5 mg/L at 32° still retained a 1 mg/L residual at the end of seven days.

Ozone dissipation data are presented in Table 47 and Figures 71, 72, and 73. Ozone depletion at 8° and 16°C was uniform at the doses chosen with very little difference between temperatures. The rate of dissipation varied from approximately 0.07 to 0.14 mg/L-min. At higher temperatures ozone dissipation was much more rapid, particularly during the first few minutes after addition. Presumably, this is due to the decreased solubility of ozone at high temperatures as well as to increased reaction rates with oxidizable dissolved substances. Low concentrations of ozone dissipated somewhat more slowly so the reaction is not entirely zero order. Under the conditions tested, ozone persisted for only a few hours at the most.

The disinfectants tested during this portion of the alternate disinfectant phase, arranged according to their ability to maintain residual concentrations are: $NH_2Cl > Cl_2 > ClO_2 >> O_3$. All of the disinfectants tested exhibited to some degree an initial demand that was greater than the

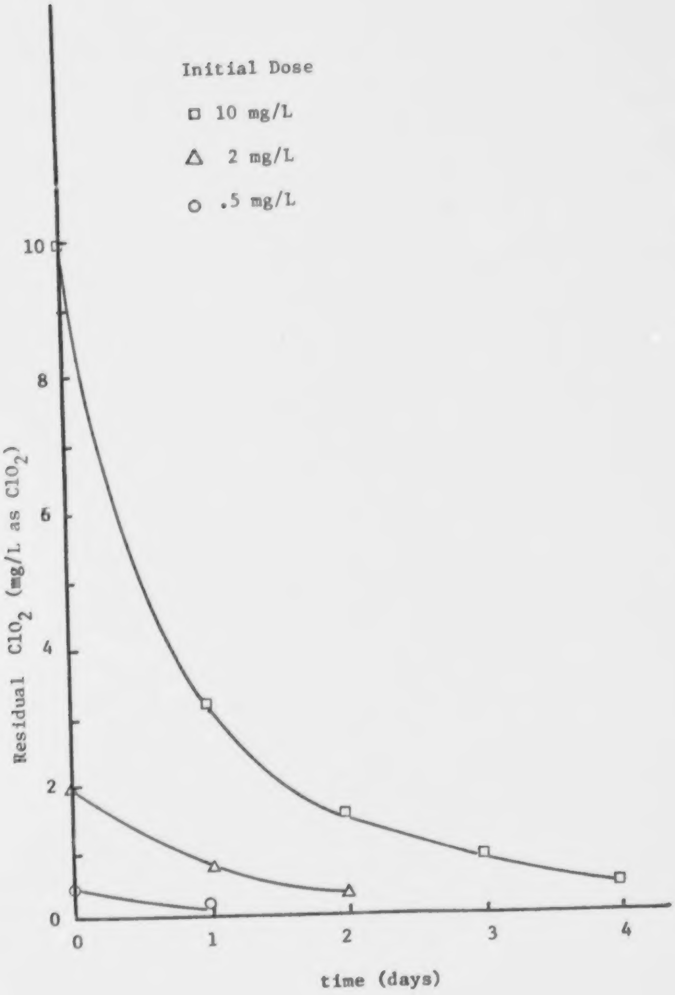


Fig. 65. ClO_2 residual vs time at 8°C.

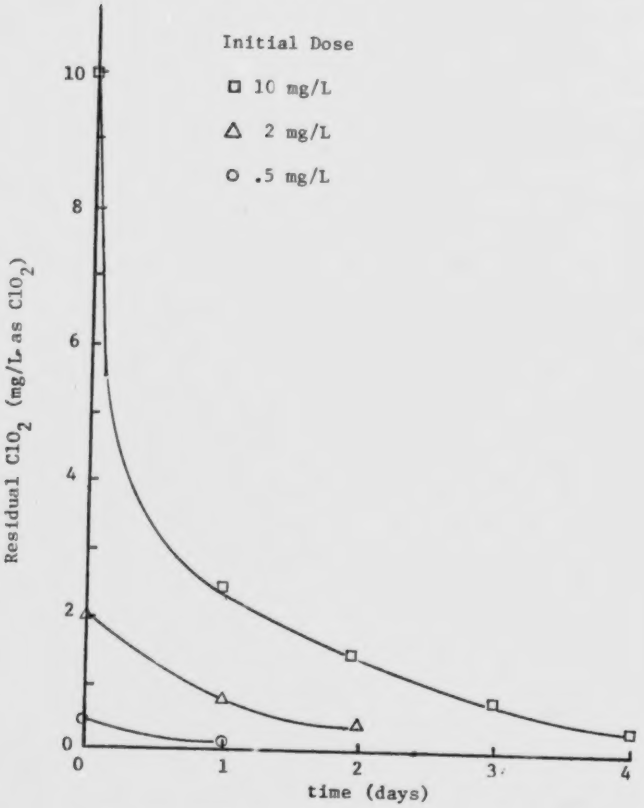


Fig. 66. ClO_2 residual vs time at 16°C.

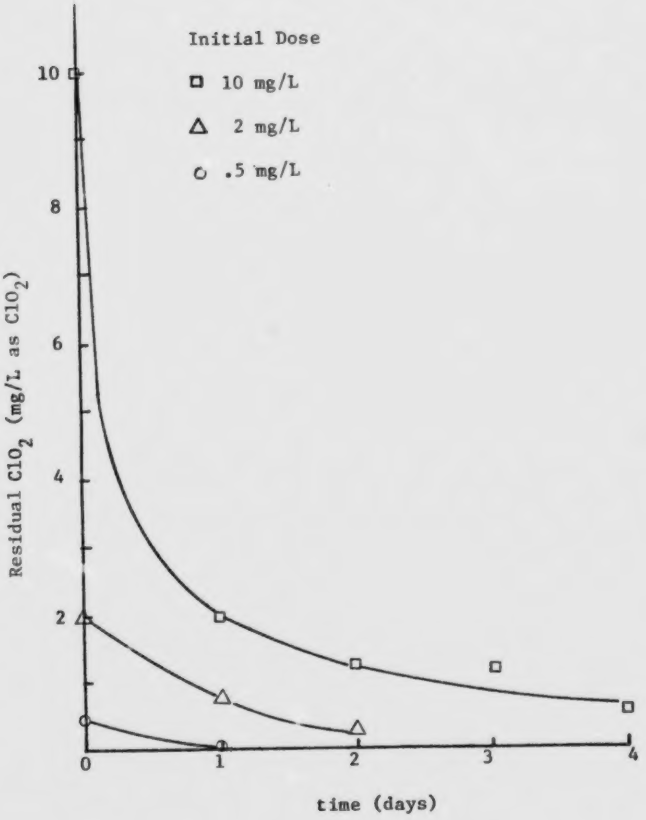


Fig. 67. ClO_2 residual vs time at 32°C.

Table 46. Chloramine Residual vs Time for Finished Melbourne Water.

Chloramine Residual (mg/L) as Cl)

Dose (mg/L)	time (days)	8°C	16°C	Dose (mg/L)	time (days)	32°C
3	0	3.0	3.0	1	0	1.0
	2	2.1	2.1		0.25	0.3
	4	1.6	1.6		1	0.1
	6	1.5	0.6		2	0
	8	0.6	---		7	0
	10	---	---			
	12	---	---			
	14	---	---			
6	0	6.0	6.0	3	0	3.0
	2	4.5	5.0		0.25	1.7
	4	2.9	4.7		1	1.1
	6	2.0	3.0		2	0.8
	8	1.6	1.9		7	0.1
	10	0	0.6			
	12	---	---			
	14	---	---			
12	0	12.0	12.0	5	0	5.0
	2	10.1	10.0		0.25	3.2
	4	9.0	8.0		1	2.4
	6	6.6	7.0		2	2.0
	8	5.0	5.8		7	1.0
	10	2.5	3.0			
	12	1.5	0.5			
	14	---	---			
25	0	25.0	25.0	10	0	10.0
	2	21.5	23.0		0.25	7.2
	4	17.5	19.0		1	6.5
	6	13.0	16.0		2	5.5
	8	8.4	9.8		7	3.7
	10	5.2	6.5			
	12	2.5	3.0			
	14	1.5	1.7			

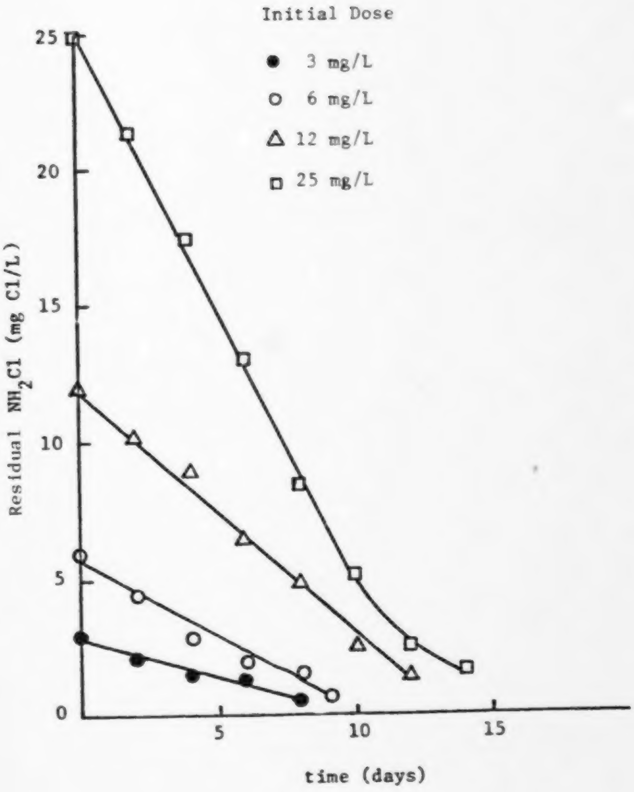


Figure 68 Chloramine Residual vs time at 8°C in finished water.

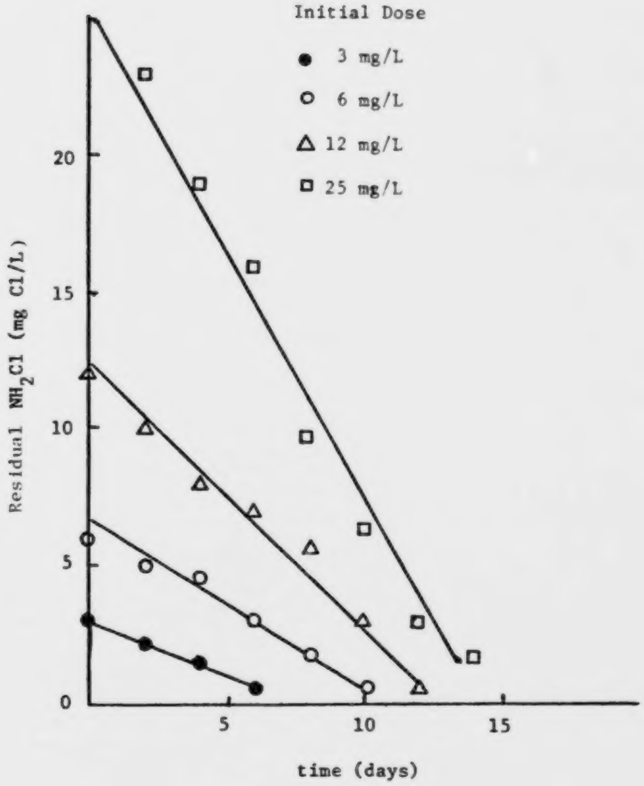


Figure 69 Chloramine residual vs time at 16°C in finished water.

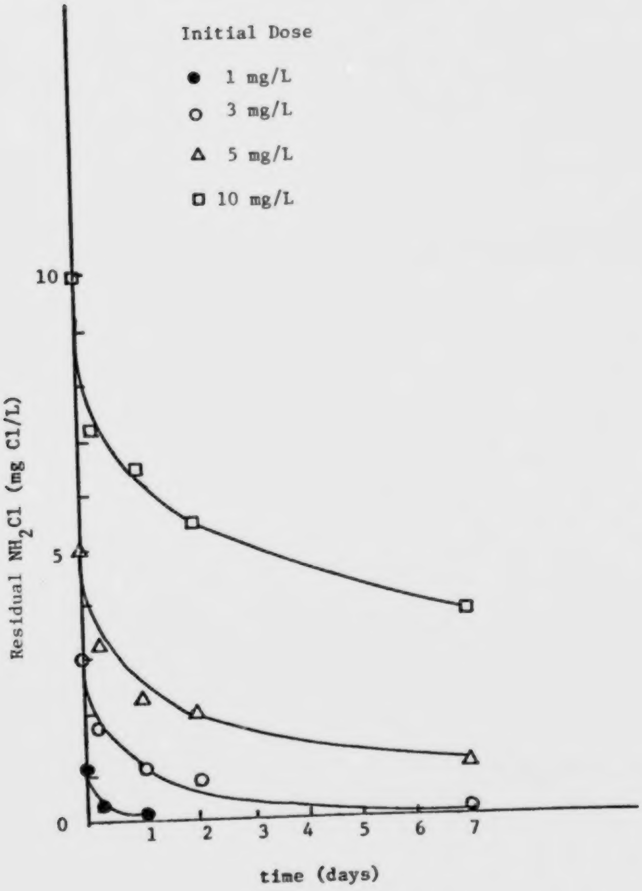


Figure 70 Chloramine residual vs time at 32°C.

Table 47. Ozone Residual vs time for Finished Melbourne Water.

		Ozone Residual (mg/L as O_3)				
O_3 Dose (mg/L)	time (min)	8°C	16°C	O_3 Dose (mg/L)	time (min)	22°C
2	0	2.0	2.0	5.7	0	5.7
	10	1.5	2.0		2.5	1.1
	15	1.0	0.8		5	.9
	20	0.7	0		10	.6
	25	0.2			30	.3
	30	0			60	.2
5	0	5.0	5.0			
	10	3.9	4.0			
	15	3.5	3.6			
	20	2.2	2.5			
	25	1.5	1.7			
	30	0.7	1.0			
	50	0	0			
10	0	10.0	10			
	10	8.3	7.3			
	15	6.0	6.7			
	20	5.2	5.8			
	25	4.0	5.0			
	30	2.7	4.5			
	50	2.0	2.0			
	60	1.8	1.5			
	70	0.6	0.9			

*Ozone dissipation was not measured at 32°C due to equipment malfunction.

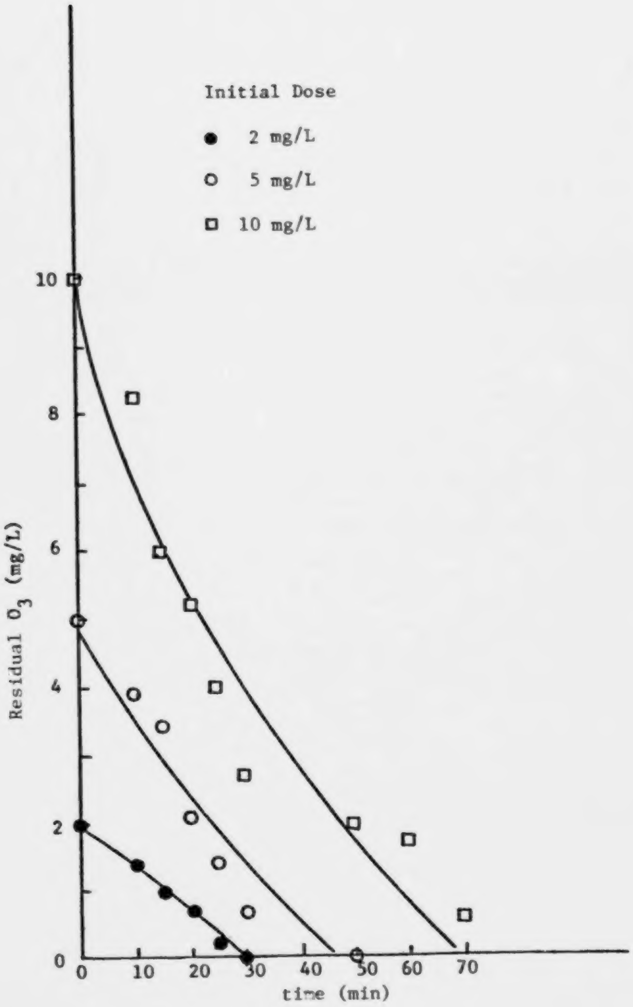


Figure 71 O_3 Residual vs time at 8°C.

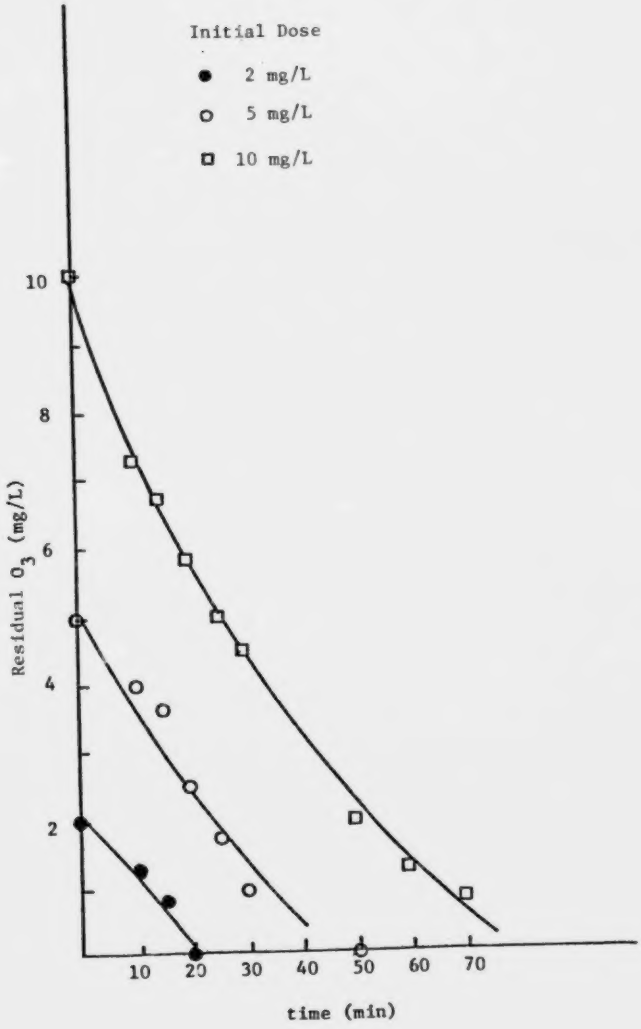


Figure 72 O_3 Residual vs time at 16°C.

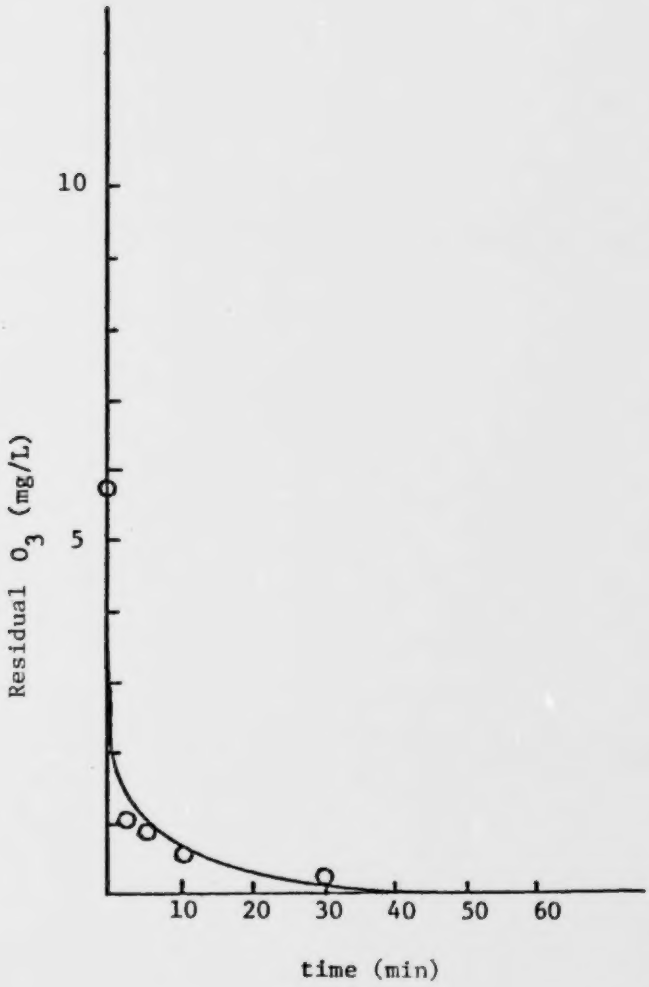


Figure 73 O_3 **Residual vs time at** 22°C. Initial dose = 5.8 mg/L.

dissipation rate at later times. In the cases of monochloramine the initial demand was most noticeable at elevated temperature. Ozone also dissipated more rapidly at higher temperatures, however, this may be because of decreased solubility at higher temperature. Only monochloramine was able to maintain a minimum residual of 0.6 mg/L for as long as seven days using a reasonably low dose. At 32°C a dose as low as 5 mg/L maintained a residual for seven days. Chlorine might maintain a residual for seven days at 32°C but only with a dose in excess of 40 mg/L. Such high doses are not desirable for economic as well as water quality reasons.

7.6.3 Water Quality After Single Disinfectant Addition

In this section, the effect of single disinfectant addition on water quality was determined. Water samples were taken at the Melbourne Water Treatment Plant at a point following filtration and preceding chlorine addition. Varying doses of each of the disinfectants (chlorine, chlorine dioxide, monochloramine, and ozone) were added to one liter samples of the finished Melbourne water. These were incubated at either 8°, 16°, or 32°C for fourteen days or until a specified minimum disinfectant residual was reached. The minimum residual was 0.6 mg/L for monochloramine and 0.5 mg/L for the other disinfectants. At the minimum residual or fourteen days, the following water quality parameters were measured: TOC, color, InstTHM, TermTHMFP and SPC. These values were then compared with the parameters for raw and finished water. These data are presented in Tables 48, 49 and 50.

Chlorine reduced SPC to zero organisms/100 mL for all doses at 8°C and 16°. At 32°C lower doses of chlorine did not result in complete disinfection, however, the number of organisms/100 mL were still low enough to be indicative of high water quality. Color removal by chlorine ranged from 30% to 65% at 8°, 25% to 60% at 16°, and 41% to 83% at 32°. The only dose to lower color to less than 5 cpu was 25 mg/L at 32°C. The TOC concentration was reduced by about 1 to 2.0 mg/L from the finished water. A minimum residual of 0.5 mg/L was maintained for seven days or more by an initial dose of 4 mg/L or greater. These results contrast with results from the dissipation section above. This difference was probably due to the difference in starting water quality.

Trihalomethanes were formed during the initial exposure to chlorine. The InstTHM concentrations were proportional to the chlorine dose. TermTHM concentrations were higher than the InstTHM concentrations. This indicates

Table 48. Effect of Single Disinfectants on Lake Washington Water at 8°C.

Disinfectant	Dose (mg/L)	T_R [1] (days)	TOC (mg/L)	Color (cpu)	InstTHM [2] (μg/L)	TermTHM [3] (μg/L)	SPC (#/100mL)
Raw	--	--	20.4	63	0	943	>100,000
Finished	--	--	11.4	24	0	207	1670
O_3	3	25 min	9.7	13	0	139	0
	5	35 min	9.6	10	0	151	0
	5	35 min	9.6	12	0	167	0
	10	80 min	9.5	8	0	145	0
ClO_2	0.5	1	10.8	19	0	140	0
	2.0	2	10.8	14	0	137	0
	2.0	2	10.9	17	0	152	0
	10.0	4	10.6	8	0	153	0
Cl_2	2	3	9.7	17	93	214	0
	4	9	9.6	15	158	261	0
	8	10	9.4	12	241	392	0
	8	10	9.4	13	249	376	0
	16	12	9.4	10	362	538	0
	25	>14	9.9	7	476	621	0
NH_2Cl	3	8	10.1	24	0	101	109
	6	9	10.1	24	0	91	87
	12	13	10.1	23	0	73	53
	12	13	10.1	24	0	93	62
	25	>14	10.1	21	0	84	57

1 T_R = time to reach minimum residual.

2 InstTHM = THM concentration @ T_R.

3 TermTHM = THM concentration 48 hr after 20 mg/L Cl_2 addition at T_R.

Table 49. Effect of Single Disinfectants on Lake Washington Water at 16°C.

Disinfectant	Dose (mg/L)	T_R [1] (days)	TOC (mg/L)	Color (cpu)	InstTHM [2] (µg/L)	TermTHM [3] (µg/L)	SPC (#/100mL)
Raw	--	--	19.3	61	0	837	TNTC
Finished	--	--	11.0	22	0	192	1470
O_3	3	25 min	10.0	9	0	117	0
	5	35 min	9.3	6	0	109	0
	5	35 min	9.5	6	0	104	0
	10	75 min	9.4	5	0	114	0
ClO_2	0.5	1	11.0	17	0	123	21
	2.0	2	10.0	13	0	130	0
	10.0	4	10.2	12	0	128	0
	10.0	4	10.2	13	0	137	0
Cl_2	2.0	3	9.0	15	81	188	0
	4.0	8	9.5	14	127	189	0
	8.0	9	9.8	12	186	269	0
	8.0	9	9.6	10	172	233	5
	16.0	11	9.3	11	238	329	0
	25.0	>14	9.8	9	393	594	0
NH_2Cl	3	6	10.1	18	0	117	55
	6	10	10.1	19	0	94	34
	12	13	10.4	19	0	97	8
	12	13	10.1	20	0	85	14
	25	>14	10.3	20	0	62	13

[1] T_R = time to reach minimum residual.

[2] InstTHM = THM concentration @ T_R.

[3] TermTHM = THM concentration 48 hr after 20 mg/L Cl_2 addition at T_R.

Table 50. TOC, Color, Standard Plate Count, and Time to Minimum Residual for Single Disinfectants at 32°C.

Disinfectant	Dose (mg/L)	T_R[1] (days)	TOC (mg/L)	Color (cpu)	InstTHM[2] (µg/L)	TermTHM[3] (µg/L)	SPC (#/100mL)
Finished Day 7	--	--	10.0	26	0	159	1580
Finished Day 14	--	--	10.8	24	0	70	1795
O_3	3	<1	10.0	12	0	90	0
	5	<1	10.7	11	0	136	0
	5	<1	10.6	11	0	130	0
	10	<1	10.3	8	0	160	0
ClO_2	0.5	1	10.2	17	0	160	18
	2.0	2	10.4	16	0	81	0
	2.0	2	10.5	16	0	92	0
	10.0	4	10.1	6	18	60	0
Cl_2	2.0	5	10.5	14	43	81	6
	4.0	10	10.1	8	81	106	12
	8.0	11	9.9	7	195	200	3
	8.0	11	9.7	7	183	207	0
	16.0	11	10.0	6	257	294	0
	25.0	>14	9.3	4	370	406	0
NH_2Cl	3.0	8	10.1	23	0	70	210
	6.0	11	10.0	21	0	70	132
	12.0	11	10.2	22	0	70	119
	12.0	14	11.0	20	0	68	87
	25.0	>14	11.1	17	0	81	0

1 T_R = time to reach minimum residual (days).

2 InstTHM = THM concentration @ T_R.

3 TermTHM = THM concentration 48 hr after addition of 20 mg/L Cl_2 at T_R.

that the initial chlorine dose was not sufficient to react with all of the precursor substances present in the finished water. In these experiments, InstTHM's produced during the initial exposure to free chlorine ranged from 43% to 97% of the TermTHM's. Smaller differences between InstTHM and TermTHM were noted at 32° then at 16° and 8°. This could be caused by more efficient InstTHM production during the initial exposure to chlorine at higher temperatures. Table 50 shows that TermTHM decreased by 56% in the finished water between day 7 and 14. This suggests that TermTHM decreased with time of storage before chlorination possibly due to biological action. These, however, do not explain the generally lower TermTHM results at 32° compared to 8° and 16°. This may be caused by the increased demand of competing reactions at the higher temperature.

Ozone gave excellent results as a disinfectant, reducing SPC to less than 1/100 mL at all doses and temperatures. InstTHM concentrations in the ozone treated water were zero at all doses and temperatures. Color was reduced from 24 cpu in the finished lake water to as low as 5 cpu (10 mg/L at 16°C). A 5 mg/L ozone dose oxidized color to 6 cpu at 16°C and about 11 cpu at 8 and 32°C. As was the case with ozone in the previous color reduction studies, color reduction by ozone was generally better at 16°C than at 8° or 32°. TermTHM's were reduced by 25% and 40% at 8° and 16°C respectively, however the reduction was less at 32°C. The decreased efficiency of ozone at higher temperatures may be indicative of lower ozone solubility or competing reactions. The TOC concentration was reduced by almost 2 mg/L at 8°C, about 1.5 mg/L at 16°C, and about 0.2 mg/L at 32°C.

Chlorine dioxide reduced the standard plate count to less than 1/100 mL with 2 and 10 mg/L doses at all temperatures. Using a 0.5 mg/L dose, SPC was reduced by 99% at 8° and 16°C. At 32°C SPC was also reduced to less than 1/100 mL by 0.5 mg/L ClO_2. Color reduction by ClO_2 was greatest at 8° and 32°C. At 16°C there was little or no difference between 2 and 10 mg/L for color reduction. This may have been due in part to the color added by ClO_2 itself. The lowest color produced by ClO_2 was 6 cpu for 10 mg/L at 8°C. Doses of 2 mg/L were generally sufficient to reduce color to 15 cpu. The TOC concentration was reduced only slightly, if at all by ClO_2 addition. Minimum residuals were maintained for one, two, and four days by 0.5, 2.0, and 10 mg/L doses respectively at all temperatures.

InstTHM's were not formed by ClO_2 at 8 or 16°C. At 32°C, 18 µg/L were formed in the sample treated with 10 mg/L ClO_2. This was the only case in which ClO_2 was found to produce THM's. ClO_2 addition decreased TermTHM by 30% to 40% at 8° and 16°C. At 32°C, TermTHM was reduced by as much as 50% compared to the 7 day control.

Monochloramine was the least effective of the disinfectants at reducing standard plate count. SPC reduction ranged from 93 to 97% at 8°C, 96 to 99% at 16°C and 88% to 100% at 32°C. Monochloramine was also the least effective for color reduction. The lowest color resulted from a dose of 25 mg/L at 32°C which produced a color of 17 cpu (29% reduction). The TOC concentration was decreased slightly during chloramine treatment, usually less than 1 mg/L. The time to reach a minimum residual (0.6 mg/L) was longer for monochloramine than for any of the other disinfectants. The minimum time to reach this residual was for a 3.0 mg/L dose at 16°C, which lasted for six days.

InstTHM's were not formed by chloramines at any dose or temperature. In addition, chloramine use inhibited the formation of TermTHM when chlorine was added at a later point. This is indicated by decreasing TermTHM with increasing chloramine dosage. TermTHM reduction ranged from 0 to 68% relative to the control. The inhibition of TermTHM formation was noticeably greater at 8° and 16°C than at 32°C.

The best single disinfectant for control of TermTHM was monochloramine. Both chlorine dioxide and ozone produced little or no InstTHM's and slightly reduced TermTHM, but to a lesser degree than monochloramine. Color removal was best accomplished by ozone and chlorine whereas monochloramine reduced color only slightly. Monochloramine retained a disinfectant residual longer than any of the other disinfectants. Neither ozone nor chlorine dioxide could retain a minimum residual for seven days, the maximum residence time expected in the Melbourne distribution system. Finally, all of the disinfectants tested reduced the standard plate count from 90 to 100%. Ozone, chlorine dioxide, and chlorine were approximately equal in this regard. Monochloramine was less effective at reducing standard plate count.

7.6.4 Alternate Disinfectant Pairs

This section describes the results of treating finished Melbourne water with combinations of alternate disinfectants. The primary disinfectant was added to water and allowed to react for thirty minutes. After this period, the secondary disinfectant was added and the sample incubated at the specified temperature for up to fourteen days. At this point, water quality parameters including color, TOC, InstTHM, and TermTHM were measured. The disinfectant pairs were (primary-secondary): ozone-chlorine dioxide, ozone-monochloramine, chlorine-monochloramine, and chlorine dioxide-monochloramine.

Table 51 gives the results of tests using ozone as the primary disinfectant and chlorine dioxide as the secondary disinfectant. ClO_2 doses from 0 to 2.0 mg/L appeared to have little if any effect on TermTHM at any of the temperatures tested. The control concentration at 16°C was 465 μg/L which was not significantly different from results obtained with ozone alone or ozone and ClO_2. The most important factor controlling TermTHM was temperature as the concentration more than doubled between 8° and 32°C.

Color was reduced by ozonation from 15 to 12 cpu. No further color reduction was achieved by chlorine dioxide addition. InstTHM's, which were absent in the control, were present in samples treated with ozone and ClO_2 at a concentration of about 10 μg/L. The TOC concentration was reduced by less than 1 mg/L in most combinations of ozone and ClO_2 when compared to the control. No pattern of TOC reduction was noticeable from these data.

The minimum ClO_2 residual of 0.5 mg/L was reached within 24 hours by all doses at all temperatures. From a practical standpoint, the use of O_3-ClO_2 combinations at these doses are therefore precluded. These results are similar to corresponding doses and temperatures for single disinfectants. In the single disinfectant section, ozone alone at 3 mg/L reduced color to between 9-13 cpu. Chlorine dioxide reduced color as low as 13 cpu at similar doses. In the combined disinfectant tests, it appeared that ozone was primarily responsible for color removal.

Data for the ozone-monochloramine alternate disinfectant pair are shown in Table 52. Color was reduced from 15 cpu in the finished water to 12 cpu in the ozone treated water at all three temperatures. No further color reduction occurred with the addition of monochloramine. These results are consistent with results obtained from single disinfectants. Temperature had no effect on color removal by ozone or monochloramine.

The time to reach minimum residual (T_R) was six days for the 3 mg/L sample at 32°C. All other samples with added monochloramine retained the minimum residual for fourteen days or longer. The results were comparable

Table 51. Alternate Disinfectant Pairs Data.
Primary = Ozone Reaction time = 30 minutes
Secondary = Chlorine Dioxide

Temperature (°C)	O_3 (mg/L)	ClO_2 (mg/L)	TR (days)	Color (cpu)	TOC (mg/L)	InstTHM (µg/L)	TermTHM (µg/L)
8	1.4	0	0	12	14.6	10	330
		0.5	<1	12	15.3	10	342
		1.0	<1	12	14.3	10	329
		2.0	<1	12	14.5	10	293
16	0.6	0	0	12	14.2	10	448
		0.5	<1	12	14.9	10	515
		1.0	<1	12	14.9	10	472
		2.0	<1	12	13.9	10	493
32	0.9	0	0	12	14.9	10	691
		0.5	<1	12	14.4	10	688
		1.0	<1	12	14.5	10	722
		2.0	<1	12	14.6	10	773
16	Finished Water Control	--	--	15	15.0	0	465
16	Raw Water Control	--	--	125	33.0	0	1355*

*60 mg/L Cl_2 added to measure TermTHM in raw water samples.

T_R > time to reach minimum residual.

Table 52. Alternate Disinfectant Pairs Data.
Primary = Ozone Reaction time = 30 minutes
Secondary = Monochloramine

Temperature (°C)	O_3 (mg/L)	NH_2Cl (mg/L)	TR (days)	Color (cpu)	TOC (mg/L)	InstTHM (μg/L)	TermTHM (μg/L)
8	1.2	0	0	12	13.8	<5	286
		3.0	<14	12	14.4	<5	42
		6.0	<14	12	14.1	<5	25
		12.0	<14	12	13.8	<5	12
		25.0	<14	12	13.7	<5	10
16	4.8	0	0	12	13.9	<5	--
		3.0	<14	12	14.7	<5	40
		6.0	<14	12	14.5	<5	21
		12.0	<14	12	14.2	<5	12
		25.0	<14	12	14.7	<5	10
32	2.0	0	0	12	13.8	<5	503
		3.0	6	12	14.3	<5	29
		6.0	<14	12	13.9	<5	14
		12.0	<14	12	14.2	<5	10
		25.0	<14		14.1	<5	10
8	Fin Water Cont	--	--	15	15.2	0	403
16	Fin Water Cont	--	--	15		0	428
32	Fin Water Cont	--	--	15		0	749
16	Raw Water Control	--	--	125	34.5	0	1356*

*60 mg/L Cl_2 added to determine TermTHM in raw water samples.

T_R = time to reach minimum residual.

with results for chloramine alone in the single disinfectant experiments. The TOC concentration was typically about 1 mg/L less in ozone treated water than in the control. No further reduction was found with monochloramine addition.

Trace concentrations of InstTHM's were detected in the ozone and chloramine treated samples. These InstTHM's were close to the detection limit (less than 5 μg/L) and may represent an analytical anomaly. Monochloramine clearly reduced the TermTHM concentration in the finished water. The TermTHM concentration was reduced to as little as 10 μg/L by a monochloramine dose as low as 12 mg/L. This reduction resulted from the reaction of free chlorine (used to measure TermTHM) with the chloramines and excess ammonia present. All doses of monochloramine tested reduced TermTHM to less than 100 μg/L.

The chlorine-monochloramine disinfectant pair (Table 53) produced the longest lasting residual of all the disinfectant pairs tested. In all cases the combined chlorine-chloramine residual lasted longer than fourteen days, whereas the original 5 mg/L chlorine dose was exhausted within 24 hours. Color reduction was due solely to the action of the primary disinfectant, chlorine. The 5 mg/L chlorine dose used as primary disinfectant reduced color to 10 cpu or by about 33%. InstTHM's were formed by the action of the 5 mg/L of chlorine used as the primary disinfectant. The InstTHM's once formed were not affected by monochloramine addition. TermTHM, as might be expected, was highest in those samples not treated with monochloramine. The TermTHM then decreased at each temperature with increasing chloramine dose. In this case, however, due to the initial reaction with the primary disinfectant, TermTHM levels were not consistently below 100 μg/L.

Table 54 presents results from the chlorine dioxide-monochloramine pair. This was the only case in which color reduction improved with increasing dose of the secondary disinfectant. Chlorine dioxide by itself did not reduce color compared to the control. When monochloramine was added as the secondary disinfectant color was reduced by up to 47%. Residuals for this disinfectant pair lasted over fourteen days in all cases but one. Chlorine dioxide was dissipated within 24 hours. The TOC concentration was not significantly reduced by treatment with this pair. InstTHM's were not formed by the action of the ClO_2-NH_2Cl pair. TermTHM was reduced by monochloramines by up to 98%. In all cases, monochloramine dose of 6 mg/L or greater reduced TermTHM to less than 100 μg/L.

Table 53. Alternate Disinfectant Pairs Data.
Primary = Chlorine Reaction time = 30 minutes
Secondary = Monochloramine

Temperature (°C)	O_3 (mg/L)	NH_2Cl (mg/L)	T_R (days)	Color (cpu)	TOC (mg/L)	InstTHM (μg/L)	TermTHM (μg/L)
8	5	0	0	10	13.5	146	332
	5	3	<14	10	13.7	151	169
	5	6	<14	10	13.3	163	129
	5	12	<14	10	14.7	160	146
	5	25	<14	10	13.6	156	114
16	5	0	0	10	13.8	161	490
	5	3	<14	10	13.4	156	173
	5	6	<14	10	13.1	156	164
	5	12	<14	10	13.1	155	124
	5	25	<14	10	13.1	164	115
32	5	0	0	10	13.6	116	847
	5	3	<14	10	13.6	126	169
	5	6	<14	10	12.3	129	110
	5	12	<14	10	12.8	141	100
	5	25	<14	10	12.2	120	80
16	Finished Water Control		--	15	16.0	<10	510
16	Raw Water Control	--	--	125	33.2	<10	1335

T_R = time to reach minimum residual.

Table 54. Alternate Disinfectant Pairs Data.
Primary = Chlorine Dioxide Reaction time = 30 minutes
Secondary = Monochloramine

Temperature (°C)	ClO_2 (mg/L)	NH_2Cl (mg/L)	T_R (days)	Color (cpu)	TOC (mg/L)	InstTHM (µg/L)	TermTHM (µg/L)
8	2	0	0	15	14.9	<5	232
		3	12	15	15.3	<5	121
		6	<14	10	15.5	<5	54
		12	<14	10	15.3	<5	51
		25	<14	8	15.5	<5	43
16	2	0	0	15	15.3	<5	418
		3	<14	15	15.2	<5	143
		6	<14	10	14.5	<5	65
		12	<14	10	14.5	<5	27
		25	<14	8	14.5	<5	25
32	2	0	0	15	14.5	<5	683
		3	<14	15	14.9	<5	223
		6	<14	10	14.5	<5	28
		12	<14	10	15.5	<5	12
		25	<14	8	14.5	<5	12
16	Finished Water Control	--	--	15	15.3	<5	528

T_R = time to reach minimum residual.

The most effective combination of alternative disinfectants for TermTHM reduction were combinations involving monochloramine. TermTHM was reduced to well below 100 μg/L by the O_3-NH_2Cl and ClO_2-NH_2Cl pairs and to between 100-200 μg/L by the Cl_2-NH_2Cl pair. It is unlikely that the THM precursor substances are actually altered or destroyed by these treatments. Rather the monochloramine and excess ammonia compete with the organic precursors to react with chlorine. Color reduction was best achieved by the strong oxidants used as primary disinfectants. Only in the case of ClO_2 and NH_2Cl did it appear that the secondary disinfectant actually contributed to color reduction.

InstTHM's were formed prior to the addition of the second disinfectant when free chlorine was used as the primary disinfectant. After the thirty-minute contact period, if monochloramine was added the production of THM's stopped and further additions of chlorine did not increase TermTHM levels after monochloramine addition. This would suggest the presence of excess ammonia. Based on these results, the combination of ClO_2-NH_2Cl or Cl_2-NH_2Cl would appear to be the most desirable means of reducing color, providing a long lasting disinfectant residual, and reducing THM concentrations in the treated water.

7.6.5 Alternant Disinfectant Summary

Four disinfectants, Cl_2, O_3, ClO_2 and NH_2Cl, were investigated for color removal. All the disinfectants except $NHCl_2$ could reduce the color remaining in Melbourne's finished water to 5 cpu or less. The ratio of color to disinfectant dose at which the color was reduced from approximately 25 cpu to below the 15 cpu standard was approximately 2.0 cpu/(mg/L) ClO_2, 1.5 cpu/(mg/L) Cl_2 and 1.5 cpu/(mg/L) O_3. An increase in reaction time did not effect the final color achieved by oxidation but did increase the efficiency of only ozone to 3 cpu/(mg/L) O_3. Temperature did not affect color removal. The color could not be reduced to zero by any oxidant and was difficult to reduce below 5 cpu. Monochloramine did reduce color slightly but was generally ineffective for color removal.

The rate of disinfectant dissipation was in the order of $O_3 \gg Cl_2 > ClO_2 \gg NH_2Cl$. An initial demand was exerted by the finished Melbourne water on ClO_2 and Cl_2 residuals. This demand was increased as dose was increased. The residuals of ClO_2 and Cl_2 decayed exponentially with time at all temperatures. O_3 and NH_2Cl appeared to decay exponentially only at

32°C and decay linearly at 16° and 8°C. The monochloramine disinfectant was able to maintain the required residual of 0.6 mg/L, for seven days at a 3 mg/L dose at 32°C. Maximum (10 mg/L) O_3 and ClO_2 doses were completely dissipated by thirty minutes and five days respectively. A chlorine dose of 40 mg/L was required to maintain the required 0.2 mg/L residual in these waters at 32°C for six days.

The best single disinfectant for control of THM's was monochloramine in that a required residual could be maintained and the THM regulation of 0.1 mg/L would not be violated. ClO_2 and O_3 produced little or no THM's. In the single disinfectant studies on water quality chlorine and ozone reduced color more effectively than ClO_2 or NH_2Cl. All of the disinfectants tested greatly reduced the SPC with NH_2Cl being the least effective.

Four separate combinations of disinfectants were tested. These combinations were O_3-ClO_2, O_3-NH_2Cl, Cl_2-NH_2Cl and ClO_2-NH_2Cl. The combinations of ClO_2-NH_2Cl and Cl_2-NH_2Cl were found to be the most effective for reducing TermTHM, reducing SPC, removing trace color and providing a disinfectant residual. The use of chlorine as a primary disinfectant produced between 100 and 200 μg/L InstTHM in the thirty-minute contact period. At Melbourne if chlorine were used the contact time and dose would generally have to be less than five minutes and 5 mg/L to avoid exceeding the 0.1 mg/L THM regulation.

7.7 Granular Activated Carbon

The purpose of the GAC phase was to investigate application of GAC column systems for reduction of color, TOC and THMFP. Since the instantaneous THM's were always equal to zero, the THMFP equaled the terminal THM's and is described in this section. Four different GAC systems were investigated in column studies. These systems differed only in the pretreatment of the influent to the GAC columns. Calgon F-400 was the GAC in each of these systems. The first of these systems utilized raw water for the influent. The remaining three utilized plant-treated water as influent. Two of the three column systems utilizing plant-treated water also utilized oxidation for additional pretreatment. One of these systems utilized ozone and the other utilized chlorine dioxide. These GAC systems are described as raw water-GAC, filtered water-GAC, ozone-GAC, chlorine dioxide-GAC and abbreviated as RW/GAC, FW/GAC, FW/O_3/GAC and FW/ClO_2/GAC. The plant treatment utilized consisted primarily of coagulation, settling, recarbonation and filtration. No chlorinated (disinfected) water was input to the columns. This description is very important in understanding the differences among the GAC systems.

These studies continued for 268 days for the RW/GAC and FW/ClO_2/GAC systems and for 473 days for the FW/GAC and FW/O_3/GAC systems. Two new studies were initiated on January 14, 1983 utilizing the discontinued RW and ClO_2 columns to evaluate a wood-based GAC, denoted as GAC 1, versus a coal-based GAC, denoted as GAC 2. These columns were operated for 140 days, so, in all six different GAC systems were evaluated, four on a process basis and two on a material basis.

The raw and treated water used in the GAC studies was stored in two large tanks on the plant site. Both raw and treated water was continually pumped into and out of the tanks to ensure fresh supplies. The input to storage was approximately five gpm which was much greater than the 190 gpd to feed the raw water and 190 gpd to feed each of the three treated water systems so that it was necessary to return approximately 7,000 gpd from raw water storage and return 6600 gpd from treated water storage to the plant. The tank was filled only to a height of 5' and contained approximately 6,000 gallons so the water was detained in the tank for approximately one day.

7.7.1 Pilot Plant Setup

The pilot columns were constructed for four individual systems, each consisting of three 4" x 60" glass columns in series. The column end connections were made of stainless steel and Teflon, and the columns were connected with ½" Teflon tubing. Glass, stainless steel, and Teflon were used to minimize possible organic contamination from plastic or rubber materials. Each column was charged with 6" of fine gravel followed by 24" of granular activated carbon. A sketch of a typical column set with the optional reactor is shown in Figure 74.

Initially, the columns were backwashed for three hours to remove any fines and gases. Once backwashed, the pilot plant systems were operated at a flowrate of 0.5 liters/minute (l/min.) which coincides to an empty bed contact time (EBCT) of ten minutes. A water pressure of approximately 20 pounds/square inch gage (20 psig) was applied to the first column with pressure decreasing through the columns as time progressed. Backwashing with filtered water was performed when the pressure entering the last column went below

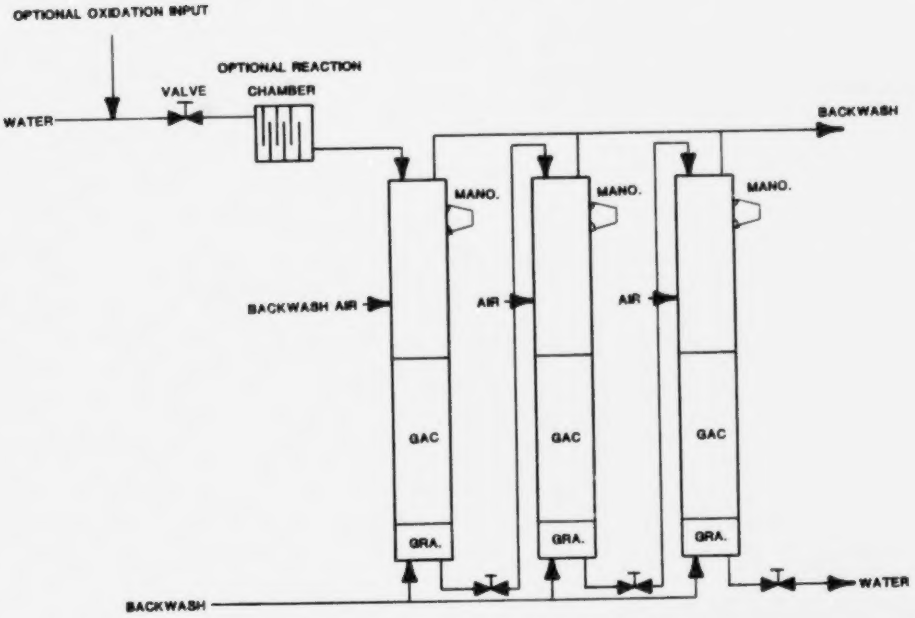

OPTIONAL OXIDATION INPUT
VALVE
OPTIONAL REACTION CHAMBER
WATER
BACKWASH
MANO.
MANO.
MANO.
BACKWASH AIR
AIR
AIR
GAC
GAC
GAC
GRA.
GRA.
GRA.
BACKWASH
WATER

FIGURE 74. PILOT PLANT GRANULAR ACTIVATED CARBON.

2-psig. In most cases, only the first column had to be backwashed, for it captured nearly all of the suspended material in the raw water.

The other GAC water systems were identical to the first except chemical pretreatment was practiced in two of them. The filtered water passed directly into a mixing tank with six baffles which allowed for a 30-minute detention time. The oxidant was added, and the mixed water was then pumped into the first column of the series.

Throughout the study, a continuous supply of O_3 and ClO_2 to the appropriate GAC system was necessary. A concentrated solution of ClO_2 was generated weekly and stored in a refrigerator. A dose of 1 mg/L was drawn from the refrigerator with a monostaltic pump and passed into the mixing tank. The ClO_2 solution was prepared as described into Section 6.2. The ClO_2 solution concentration was determined twice during the week and the pump set accordingly to maintain a 1.0 mg/L dose.

During the GAC study, ozone (O_3) was produced using a Welsbach ozonator, model T-40S, supplied with compressed air. The O_3 application rate and the O_3 concentration applied to the GAC columns were determined periodically with little variation. The O_3 application rate remained at approximately 7.0 mg/L, and the concentration of O_3 applied to the columns remained approximately 2.0 mg/L. Photographs of the GAC pilot plants are shown in Figures 75, 76 and 77.

During the study, pH, temperature color, standard plate count, TOC, and THMFP were determined. Samples for color, standard plate count, TOC, and THMFP were collected at sixteen points for analysis. Samples taken included raw water, filtered water, filtered water and O_3, filtered water and ClO_2, and the effluents of columns 1, 2 and 3 for all GAC systems. Color was measured at least twice a week throughout the study. Standard plate count was determined weekly for the first month and by every two weeks thereafter. TOC and THMFP were determined twice a week for the first month and then every two weeks for the remainder of the study. Only color, SPC, pH and temperature were measured by plant personnel. All other measurements were made by were measured by plant personnel. All other measurements were made by university personnel. Samples for pH and temperature were collected at the influent and effluent of each column system. These two parameters were measured twice a week for the duration of the study.

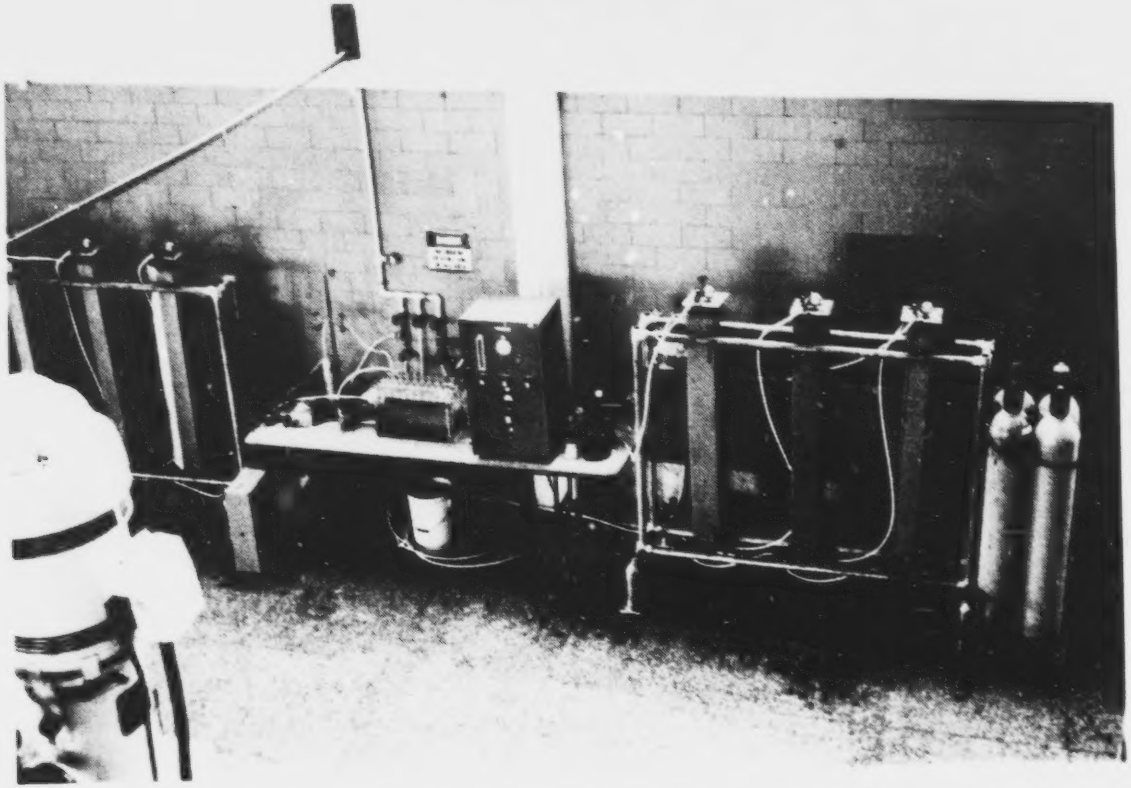


Figure 75 Photograph of Filtered Water GAC system on left and picture of Filtered Water Ozone GAC system on right showing ozonation, reactor and GAC columns

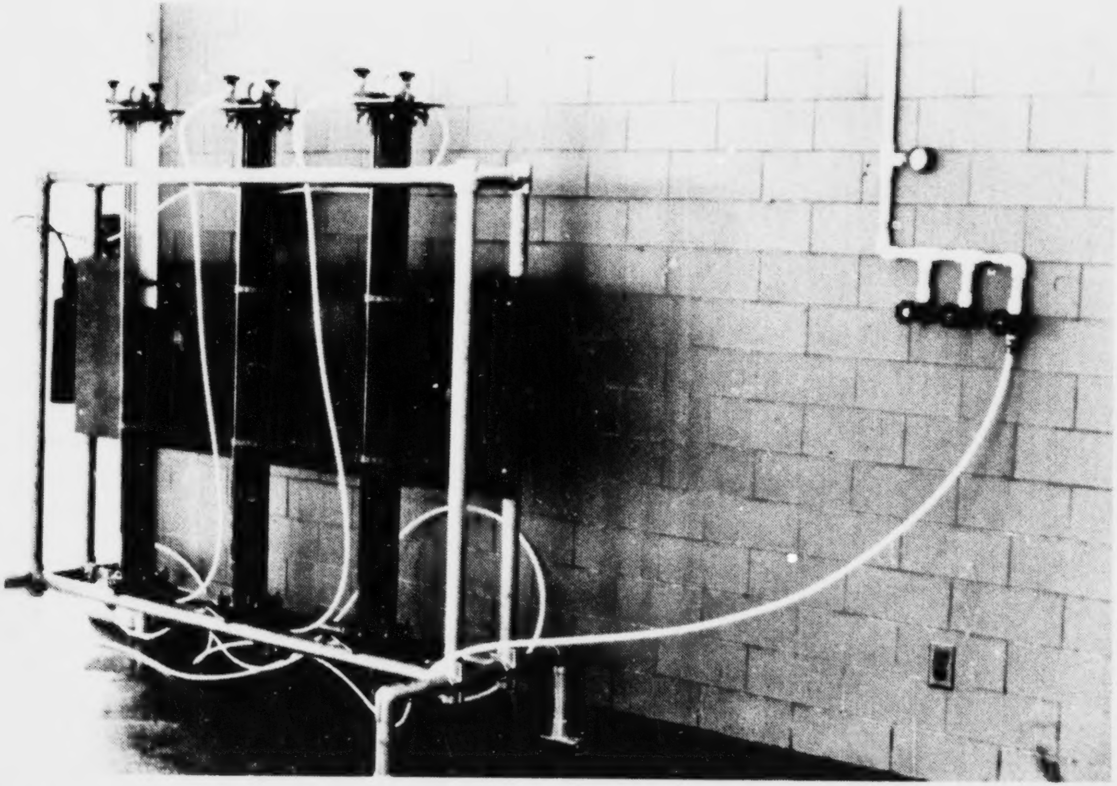


Figure 76 Photograph of Raw Water GAC system during backwash

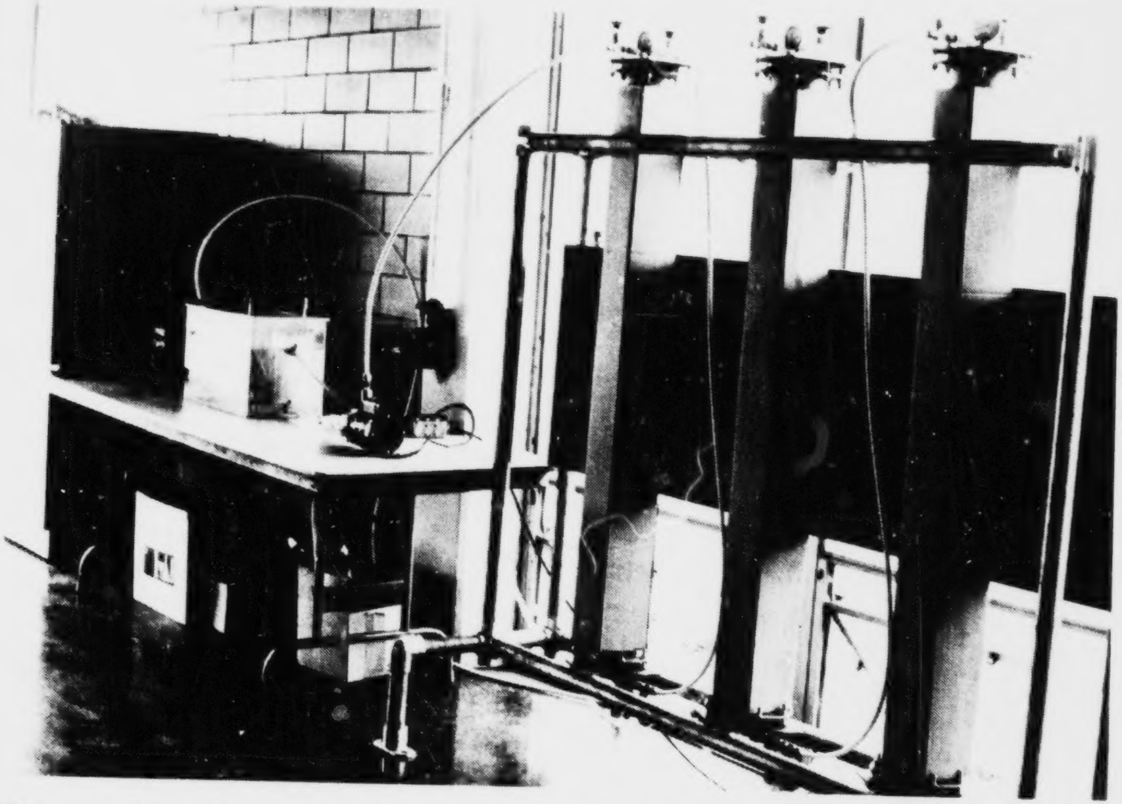


Figure 77 Photograph of Filtered Water $C10_2$ system showing $C10_2$ storage refrigerator, reactor and columns

7.7.2 Data Analysis

The THMFP, TOC, color, SPC and DO concentrations in the influent and effluent of each column in each GAC system, the ozone reactor and the ClO_2 reactor were plotted as a function of time. The influent quality varied significantly in THMFP, TOC and color due to natural variations in raw water quality and a change from high pH magnesium coagulation to alum coagulation which was more effective for THMFP, TOC and color removal.

$$\text{InstPR} = \left(\frac{C_{11} - C_{21}}{C_{11}}\right) \times 100 \qquad (8)$$

where: C_{11} = Influent concentration at time t_1, ug/L, mg/L, cpu
C_{21} = Effluent concentration at time t_2, ug/L, mg/L, cpu
InstPR = Instanteous percent removal at time t_1

$$\text{IncrePR} = \left(\frac{C_{11} + C_{12} - C_{21} - C_{22}}{C_{11} + C_{12}}\right) \times 100 \qquad (9)$$

C_{11} = Influent concentration at time t_1, ug/L, mg/L, cpu
C_{12} = Influent concentration at time t_2, ug/L, mg/L, cpu
C_{21} = Effluent concentration at time t_1, ug/L, mg/L, cpu
C_{22} = Effluent concentration at time t_2, ug/L, mg/L, cpu
IncrePR = Incremental percent removal between times t_1 and t_2, ug/L, mg/L, cpu

$$\text{CumPR} = \frac{\sum_{i=1}^{n} (\text{IncrePR})_1 (t_1 \quad - t_2)}{t_n} \qquad (10)$$

t_i = time at t_i
t_{i+1} = time at t_{i+1}
t_n = time at t_n
CumPR = Cumulative percent removal

$$\text{IncreCap} = \frac{q(t_2 - t_1)\,\frac{1}{2}\,[(C_{11} + C_{12}) - (C_{21} + C_{22}]}{M} \qquad (11)$$

where: q = flow, L/hr

t_2 = time at end of time increment, hr

t_1 = time at beginning of time increment, hr

M = mass of GAC, gm

IncreCap - Incremental Capacity cpu/gm, mg/gm

$$\text{CumCap} = \sum_{i=1}^{n} \text{IncreCap}_i \tag{12}$$

CumCap = Cumulative Capacity cpu/gm, mg/gm

The data from the GAC systems was analyzed using equations (8) through (12) and a computer. An instantaneous percent removal was determined for each sample by dividing the influent concentration into the difference between the influent and effluent concentrations as shown in equation (8). An incremental percent removal was also determined to improve accuracy. This was done by averaging the concentrations into and out of each column or the system, determining the average mass removed, and dividing it by the average mass applied for any sampling period. Time, flow, or averages do not appear in equation (9) because they were equally represented in the numerator and denominator of equation (9) and were cancelled. This was also the case in equation (10) except for time. The cumulative percent removal which represents the percent removal of mass by any columns with or the GAC system for the entire operational period. Finally an incremental GAC capacity was determined by dividing the mass removed by any column (or system) by the mass of GAC in the column (or system). This calculation is shown in equation (11) and also was summed to determine a total capacity for the entire period of operation as shown in (12). The color, TOC, and THMFP mass removals by each of the GAC system was determined and is shown in Table 55.

7.7.3 Filtered Water GAC

The results of the GAC system operating on water that had been treated by the plant treatment system are shown in Figures 78, 79, 80, 81, and 82. These figures represent the influent and effluent THMFP, TOC, color, SPC and DO concentrations for each of the three columns which are connected in series.

The GAC/FW THMFP removal of THMFP by the FW/GAC system was 97% the first three days. The THMFP concentration applied to averaged 650 ug/L during this

Table 55. Color, TOC, and THMFP removals by GAC systems at Melbourne, Florida

System	Operation (days)	Color Removed cpu x 10	TOC Removed gm x 10	THMFP Removed gm x 10
RW/GAC	268	4.08	0.95	0.08
FW/GAC	473	5.20	1.24	0.09
FW/O_3/GAC	473	6.01	1.37	0.10
O_3 only	473	2.24	0.22	0.02
FW/ClO_2/GAC	268	4.25	0.92	0.06
ClO_2 only	268	0.42	0.11	0.01
FW/GAC coal base	140	1.49	0.74	0.04
FW/GAC wood base	140	1.10	0.37	0.03

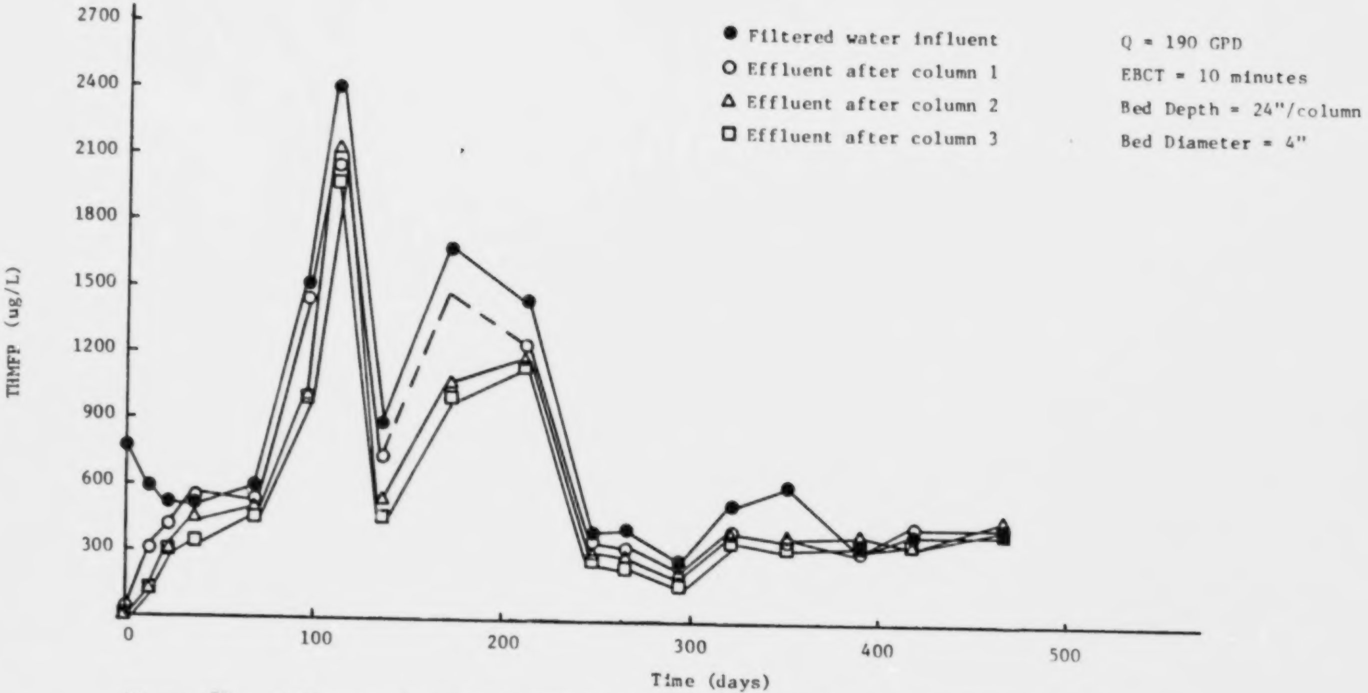


Figure 78. Influent and effluent THMFP by columns for filtered water GAC system at Melbourne.

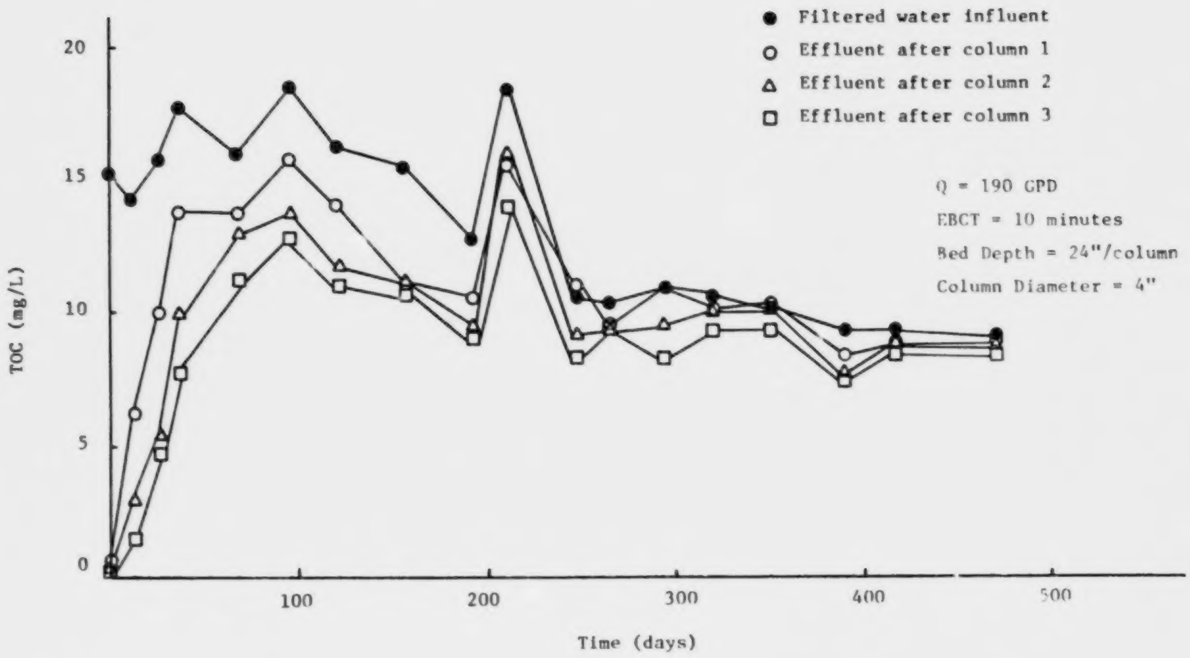


Figure 79. Influent and effluent TOC by columns for filtered water GAC system at Melbourne.

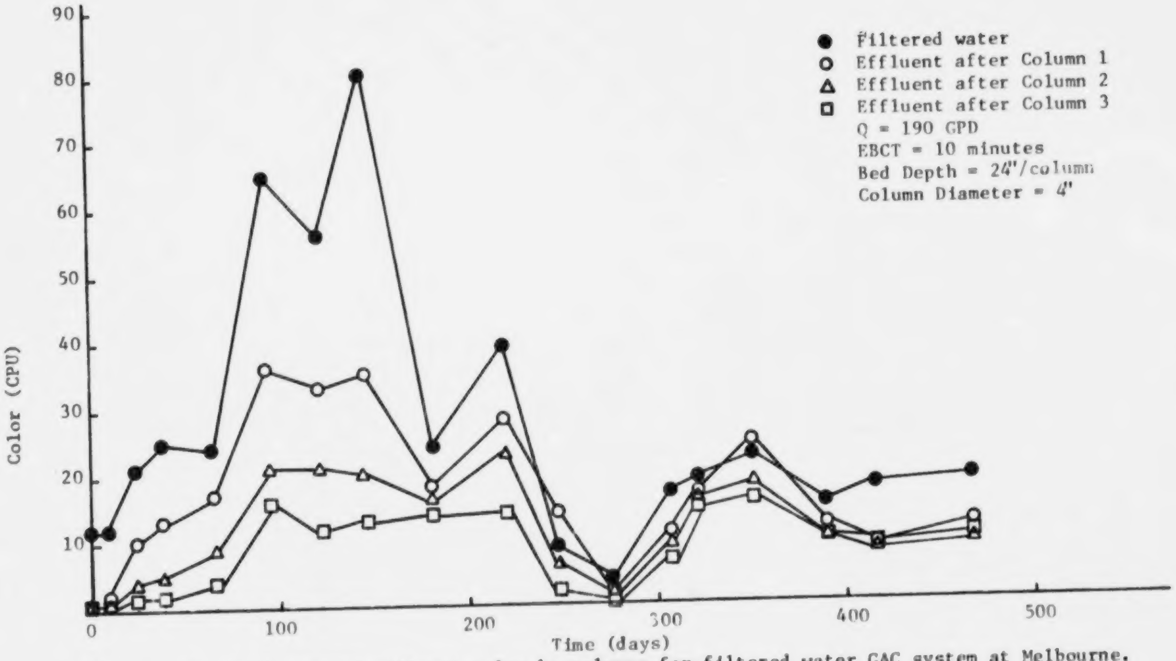


Figure 80. Influent and effluent color by columns for filtered water GAC system at Melbourne.

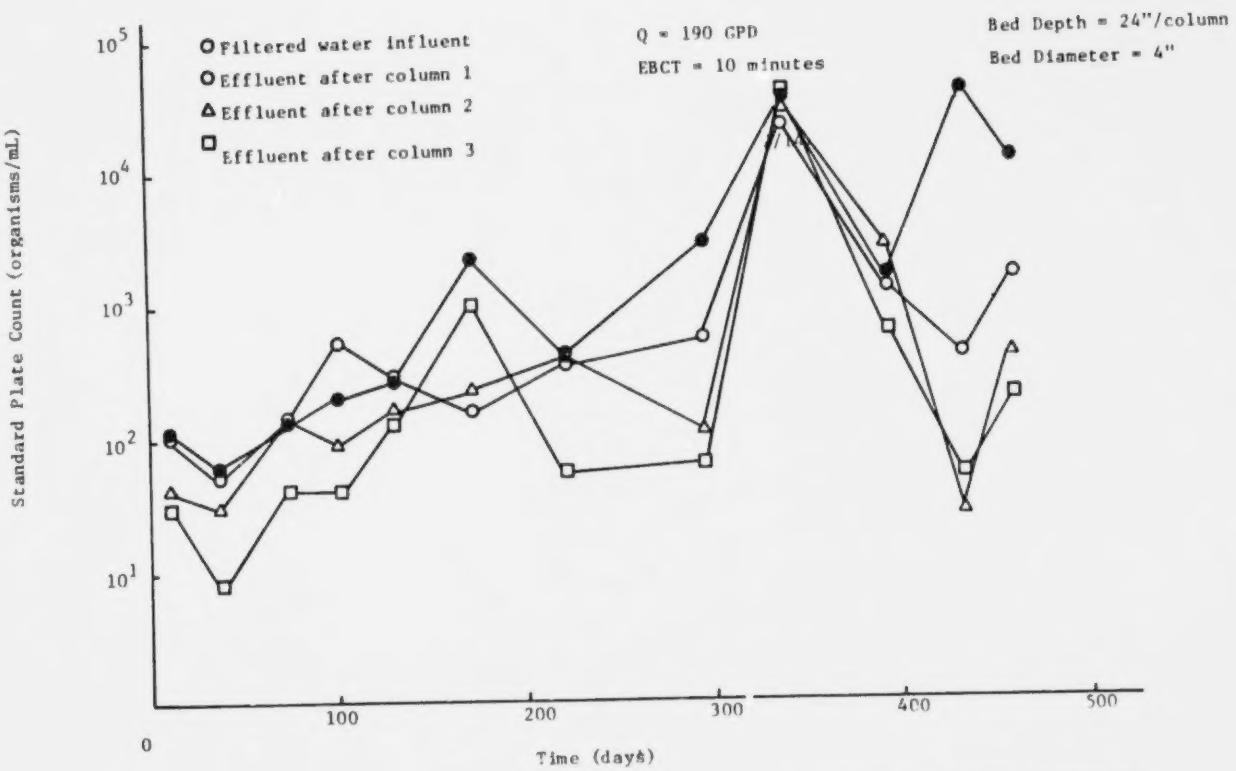


Figure 81. Influent and effluent standerd plate count by columns for filtered water GAC system at Melbourne.

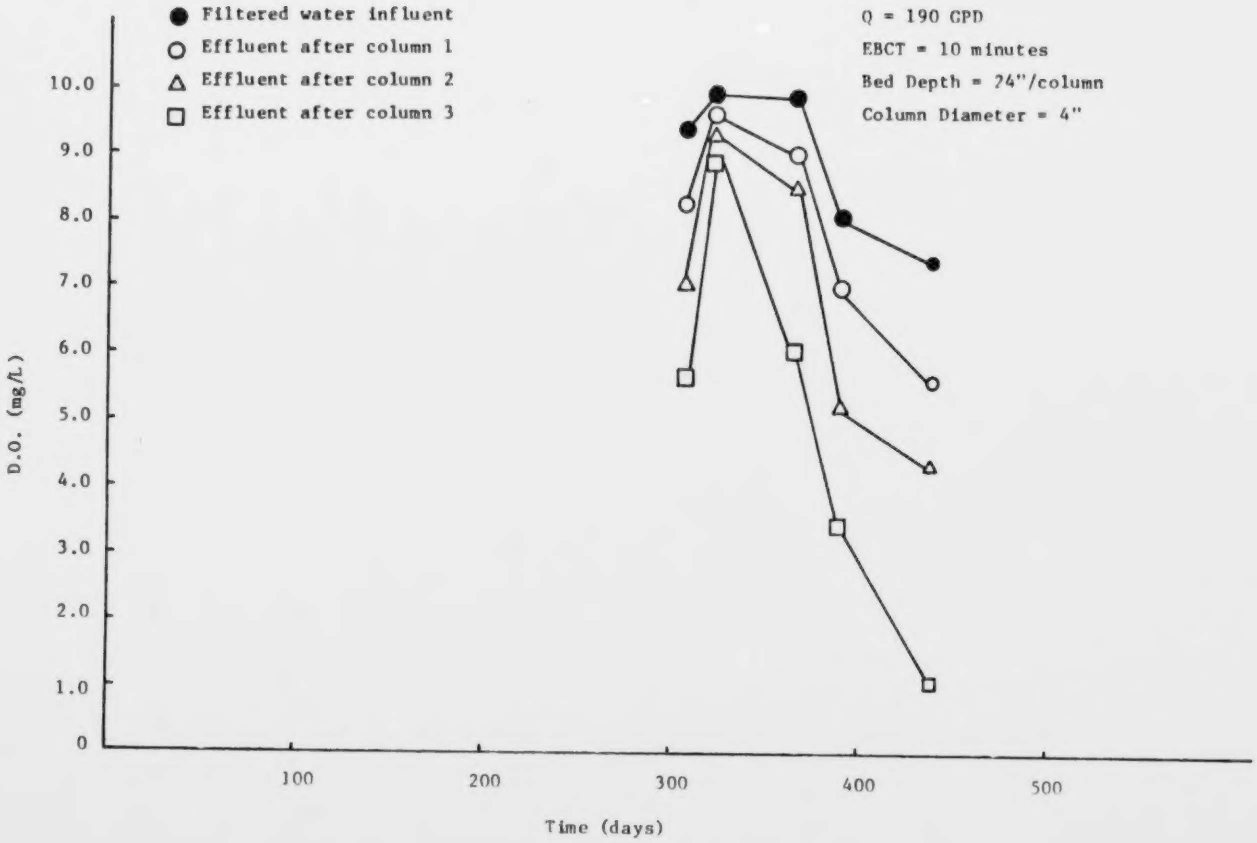


Figure 82. Influent and effluent dissolved oxygen by columns for the filtered water GAC system.

period. The effluent THMFP concentration from all columns was below 100 ug/L. As shown in Figure 78, after eight days the effluent THMFP concentration from column 1 has increased to 305 ug/L. The effluent THMFP concentrations from columns 2 and 3 have also increased to 125 ug/L. The THM regulation of 0.10 mg/L is exceeded in the effluent from all columns after 8 days of operation even though 91% or 3,324 mg of the incoming THMFP had been removed. The GAC capacity for the FW/GAC system at breakthrough to 0.10 mg/L was 0.56 mg THMFP/gm GAC. This breakthrough occurred between three and eight days of operation and is rapid considering a three-column combined EBCT of 30 minutes. The THM precursors associated with the breakthrough were poorly adsorbed by the GAC.

The total mass of TOC removed by the system was 1,244,180 gm of which 562,508 gm, 322, 778 gm and 298,893 gm were removed in columns 1, 2 and 3. The cumulative percentage of TOC removal for the system varied from 93% initially to 29% at day 473 and appeared to be approaching some limiting value of constant removal. The system THMFP removal was 86,896 gm and the system TOC removal was 1,244,180 gm. On a molar basis, using an average molecular weight of 127 for THMFP, removal of 1 mole of THMFP requires a removal of 150 moles of TOC from Melbourne's finished water.

The influent and effluent for each column in the FW/GAC system is shown in Figure 80. This figure, more than any other, shows the variability in water quality coming into the GAC systems. The raw water color was 60 cpu, which was very good for the Lake Washington source when the GAC systems were started. The finished water color of 12 cpu was as low as had been recorded during the high lime mode of operation. The raw water quality decreased and the finished color increased to 80 cpu under the different processes. After 264 days alum coagulation was employed and color decreased to below 10 cpu on occasion and always below 20 cpu even though raw water color was 200 cpu or more.

Color removal in the FW/GAC system was always significant and fell into three major periods. The variability in color removal by period may have been affected by changing raw water quality, a changing pretreatment process, saturation of the adsorbative capacities of the FW/GAC columns or combinations of these factors. It is very difficult to reliably predict bed life for color removal because of the variability of the results. For these conditions a statement relating bed capacities in cpu/gm can be made by ranges as follows.

For the first 86 days of operation a cumulative capacity of 216.7 cpu/gm GAC was observed with a minimum of 86% color removal for the FW/GAC system. During the next 167 days this capacity was increased to 690.6 cpu/gm GAC but the minimum color removal was 56%. During the final 220 days of operation this capacity was increased to 877.4 cpu/gm GAC with a minimum color removal of 20%. These data could be used to roughly estimate bed life for color removal as the FW/GAC system removed color better than TOC or THMFP and may be of use to a municipality in that regard. Alum coagulation can remove over 90% of the color from the raw water at Melbourne. The incremental percentage of color removal indicates that 30% color removal is possible after 473 days of use with no visible signs of exhaustion. Many plants using surface water supplies have to periodically treat raw colors of 200 cpu or more. Such waters reduced to 20 cpu by alum coagulation could be treated to a color less than the 15 cpu standard by GAC for more than 1.3 years before reactivation is required.

The SPC and DO concentration in the influent and effluent for each column in the FW/GAC system are shown in Figures 81 and 82. A steady increase in the SPC from the columns' effluent is generally observed for the first 300 days after which variations of 2 to 3 orders of magnitude (10^2 to 10^5 org/mL) are observed. The change from an influent that was coagulated at pH 11.5 to one that was coagulated at pH 5.5 to 6.5 greatly increased the SPC of the influent by approximately 40,000 org/mL. The SPC of the effluent generally decreases across each column although incoming SPC is observed to increase with time.

The DO concentrations decreased through each column. The DO reduction through column 3 was greater than that through column 2, which in turn was greater than that in column 1. These data indicate that biological activity was present in the columns and most active in the third column as indicated by the larger DO drop. The decrease in SPC through each column indicates that effluent SPC is probably not a good measure of the oxygen consuming species. These species were evidently attached to the carbon, out competing other species in the influent allowing them to come through the columns. The larger DO drop in column 3 was probably due to better acclimation of the bacteria because of the treatment afforded by columns 1 and 2.

The incremental of the percentage removal of THMFP, TOC and color through the FW/GAC system is shown in Figure 83. These results show a trend of

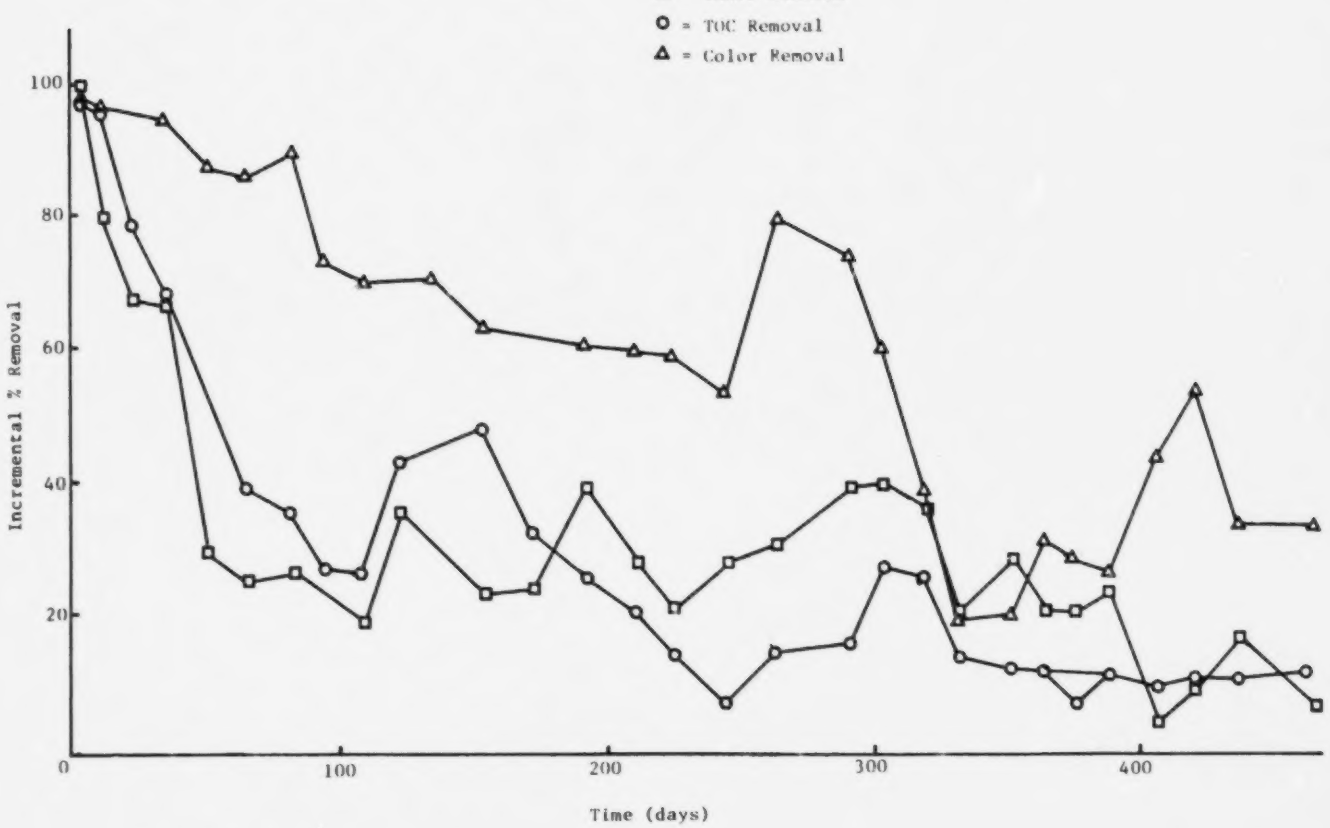


Figure 83 Incremental % THMFP, TOC, and Color removal through the Filtered Water GAC System

decreasing removal from the beginning to the end of system operation. Almost complete THMFP, TOC or color removal, > 95%, is obtained initially and decreases to 13% THMFP, 14% TOC and 34% color at the conclusion of operation. As is seen in Figure 83, color is more effectively removed by GAC than either THMFP or TOC, although a general trend of decreasing removal is apparent in all cases. This trend suggests the FW/GAC columns are slowly approaching exhaustion. The lowest removals in the FW/GAC columns occurred during the periods of the highest biological activity as indicated by SPC and DO. The largest percentage of THMFP removals occurred from day 0 to 3 (89%) for column 1, from day 0 to 3 (71%) for column 2 and from day 29 to 36 (35%) for column 3. Because of the relatively constant raw and treated water quality during this relatively short period, this suggests a "THMFP" wave breaking through the system representative of mixed organics each of which has varying GAC adsorbative capacities. Such conditions would be expected from a surface water supply.

The incremental percent removal of THMFP, TOC and color through the FW/GAC system during the 473 day operational period is shown in Figure 83. These curves are similar in that: (A) the largest percent removals were obtained initially; (B) the percent THMFP, TOC and color removals were positive; and (C) the percent removal of THMFP, TOC and color appeared to be relatively constant or very slowly decreasing after 200 to 300 days of operation. Percent TOC removal is more constant than either percent THMFP or color removal. However, the variability of percent THMFP or color removal is partially if not completely due to the analytical methods of measuring THMFP or color. Color is more readily removed by GAC than TOC or THMFP, however, there is little difference between TOC and THMFP removal.

The incremental percentage of TOC removal through each column in the FW/GAC system is shown in Figure 84. The percentage of TOC removal through each column appears to decrease until day 200 and decrease very slowly or stabilize past day 200 until the end of operation at day 473. During the final 273 days of operation the SPC into the FW/GAC system increased because of the change to alum coagulation. The DO drop across each column in the FW/GAC system increased during this period in the summer indicating biological activity. The largest DO drops were recorded after day 400 and corresponded to the smallest percentage of TOC removals as seen by comparing Figures 81

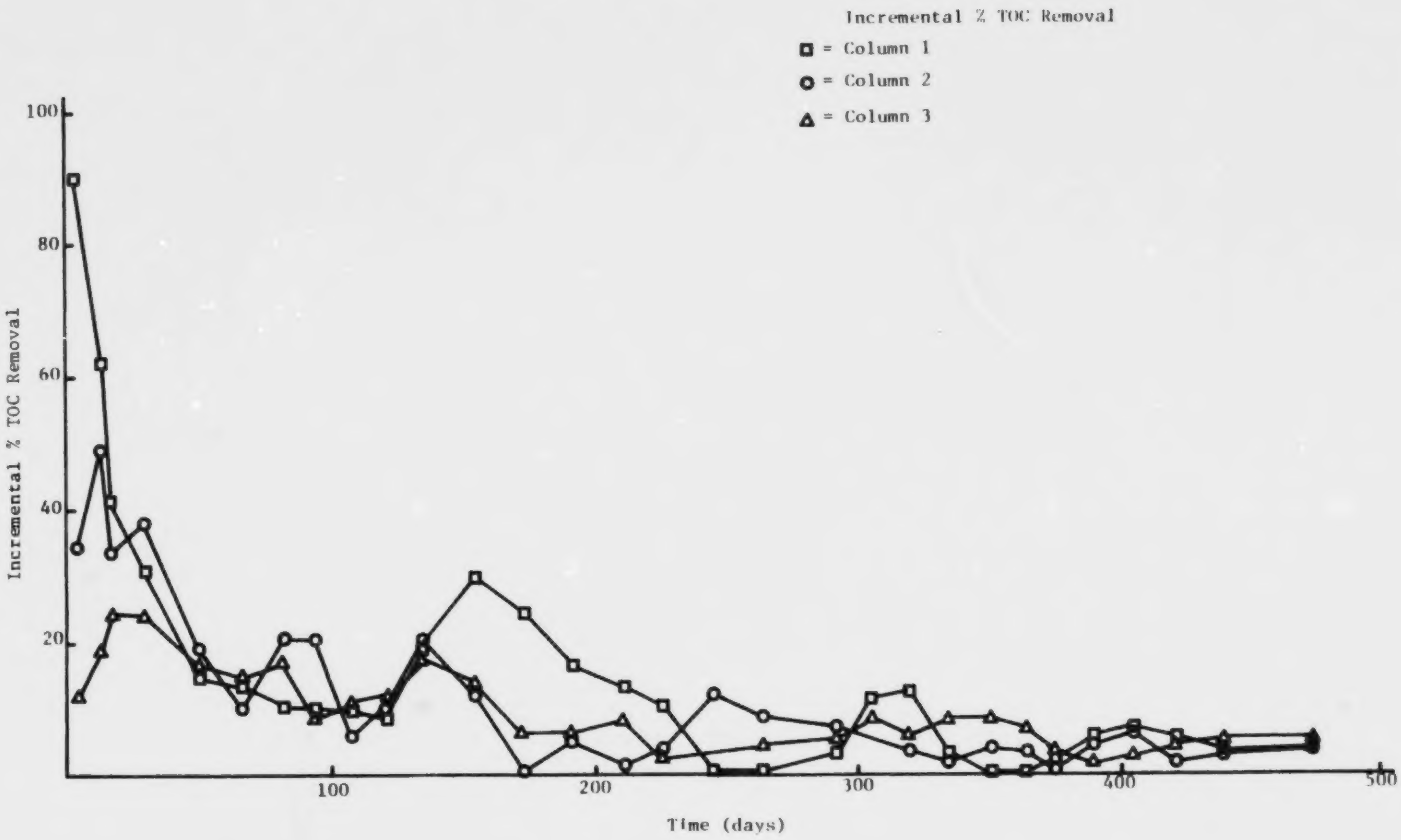


Figure 84 Incremental % Toc removal by column in the FW/GAC System

and 84. If biological activity were the major means of TOC removal in the FW/GAC columns the increased biological activity as indicated by increased DO drop would probably be accompanied by increased TOC removal. This is not the case for any column in the entire three-column FW/GAC system. The TOC removal appeared to slowly decrease through the system and the last column consistently had the largest DO drop but did not consistently produce the greatest TOC removal as shown in Figures 82 and 84.

These data suggest that physical adsorption of a mixture of organics of varying selectivity was more responsible for removal of color, TOC and THMFP in the FW/GAC system than biological activity. The highest removals of either color, TOC or THMFP always occurred initially when the GAC was unused. The change in coagulation practice from a high pH to a low pH process increased the SPC into and out of each column yet no increase in color, TOC and THMFP removal was evident. The largest decreases in DO occurred through the entire system when the highest SPC was recorded yet no increase in color, TOC or THMFP removal was observed. The capacity for THMFP and TOC removal was essentially exhausted at the end of the study in the FW/GAC system. Color removal was still occurring with no indication of exhaustion. The adsorption of all organics occurred initially with exhaustion occurring in fifty days for the organics that were poorly adsorbed. These organics would represent approximately 70% of the THMFP, 70% of the TOC and 34% of the color that was in the influent to the columns and appeared in the effluent after fifty days. The remaining 30% THMFP, 30% TOC and 66% color producing organics were highly adsorbable and removed from the effluent for the remaining 423 days. Although the number of different organics in the influent was unknown it is highly likely there were many, but these data indicate that they could be divided into classes of high and low adsorbability. Moreover these data indicate long-term removal of THMFP to 0.1 mg/L or less is not possible but long-term removal of color is possible by GAC if coagulation is used for pretreatment.

7.7.4 Ozonated Filtered Water GAC

A second GAC system was investigated using Melbourne finished water followed by ozonation before GAC adsorption. As before the THMFP, TOC, color, SPC and DO were monitored for a 473 day period through the ozone contactor and each GAC column in the FW/O_3/GAC system. The influent and effluent concentrations of THMFP, TOC, color, DO and SPC into and out of each column and the ozone contactor are shown in Figures 85, 86, 87, 88, and 89.

Ozone was dosed at 7 mg/L of which approximately 1 mg/L was utilized in the baffled contactor and 1 mg/L was applied to the first GAC column. The remaining 5 mg/L was lost in the off gas from the contactor. The contactor was baffled into six equal compartments and had a 30 minute detention time. During the pilot study the contactor was cleaned on several occasions because of biological growth and/or continuing precipitation of the treated water from the plant treatment process. The influent and effluent THMFP, TOC and color for the contactor are shown in Figures 85, 86 and 87. The application of ozone did result in an average reduction of 15.4% THMFP with a standard deviation of 9.8%, an average TOC reduction of 4.6% with a standard deviation of 58% and an average color reduction of 28% with a standard deviation of 16.5%. These reductions were variable but positive. An organic chemical reaction with ozone may have caused some of these reductions. Dark deposits or growths in the ozone contactor required frequent cleaning and likely effected these reductions. The same deposits nor removals were not found in the ClO_2 contactor.

The average reductions of THMFP, TOC and color per mg/L of applied ozone were 0.02 mg THMFP/mg O_3, and 0.09 mg TOC/mg O_3, 0.92 cpu color/mg O_3. Even considering mechanisms other than ozone, these ratios show ozone most efficiently reduced color relative to TOC or THMFP reduction. The possible mechanisms induced in the contactor are chemical oxidation, chemical precipitation or biological uptake.

The FW/O_3/GAC system produced a water that met the 15 cpu color standard for 95 days resulting in a capacity of 265 cpu/mg GAC. This system also produced a water that met the THMFP regulation of 0.10 mg/L for only eleven days resulting in a capacity of 1.04 mg THMFP/gm GAC. As with the FW/GAC system, color was better removed than TOC or THMFP which were equally removed by the FW/O_3/GAC system.

The same influent was applied to both the FW/O_3/GAC and FW/GAC systems. The FW/GAC removed a total of 5.20 x 10^6 cpu of color, 1.24 x 10^6 mg of TOC and 0.09 mg x 10^6 of THMFP. The FW/O_3/GAC system removed a total of 6.01 x 10^6 cpu of color, 1.37 x 10^6 mg of TOC and 0.10 mg x 10^6 mg of THMFP for an

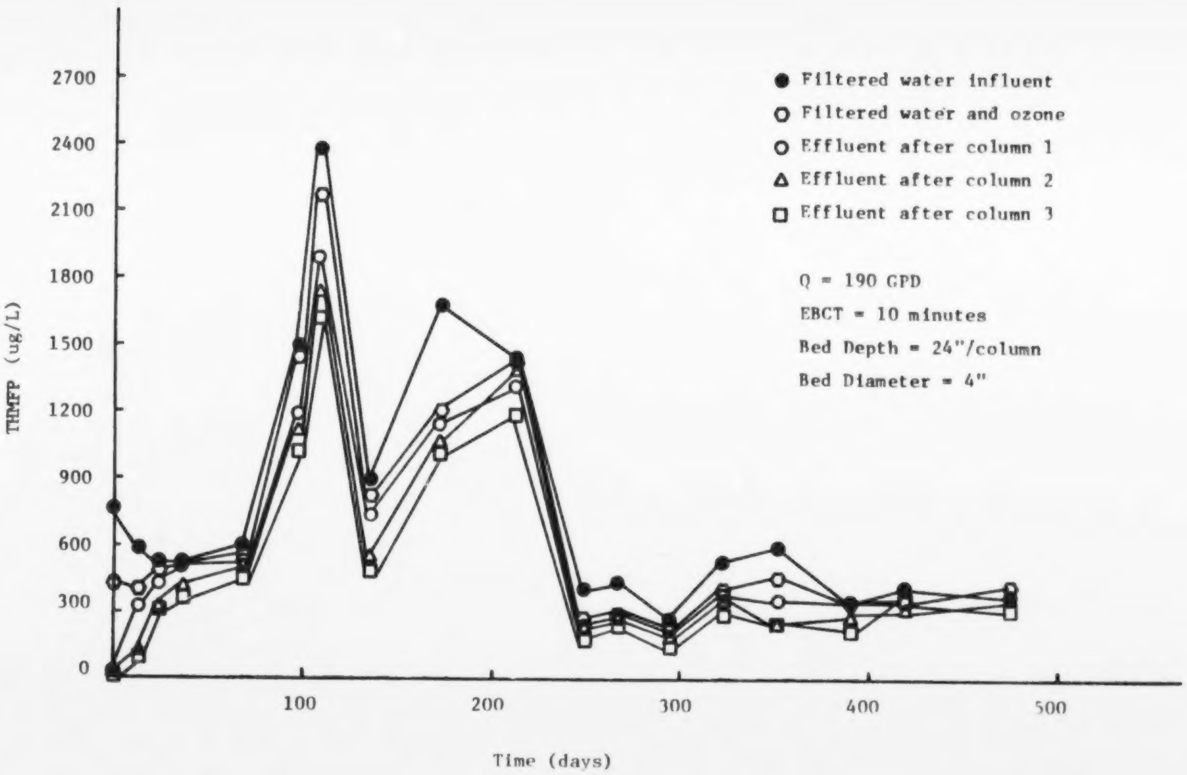


Figure 85. Influent and effluent THMFP by columns for filtered water and ozone GAC system in Melbourne.

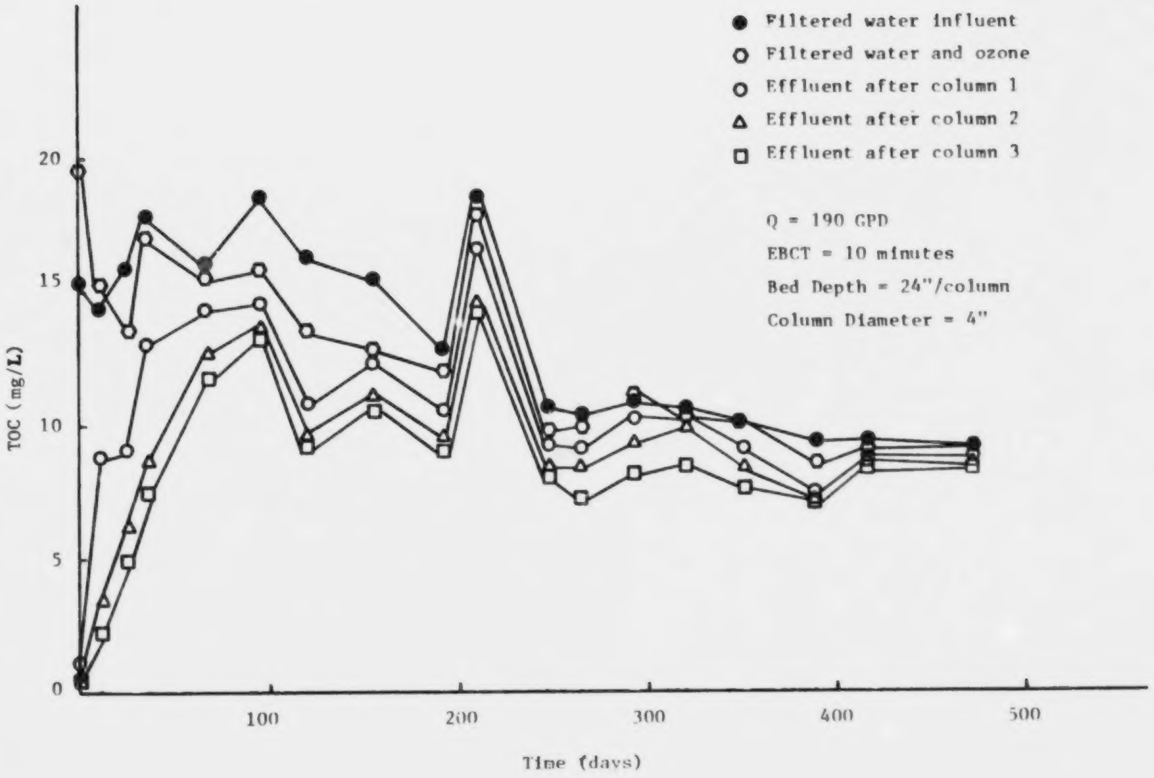


Figure 86. Influent and effluent TOC by columns for filtered water and ozone GAC system at Melbourne.

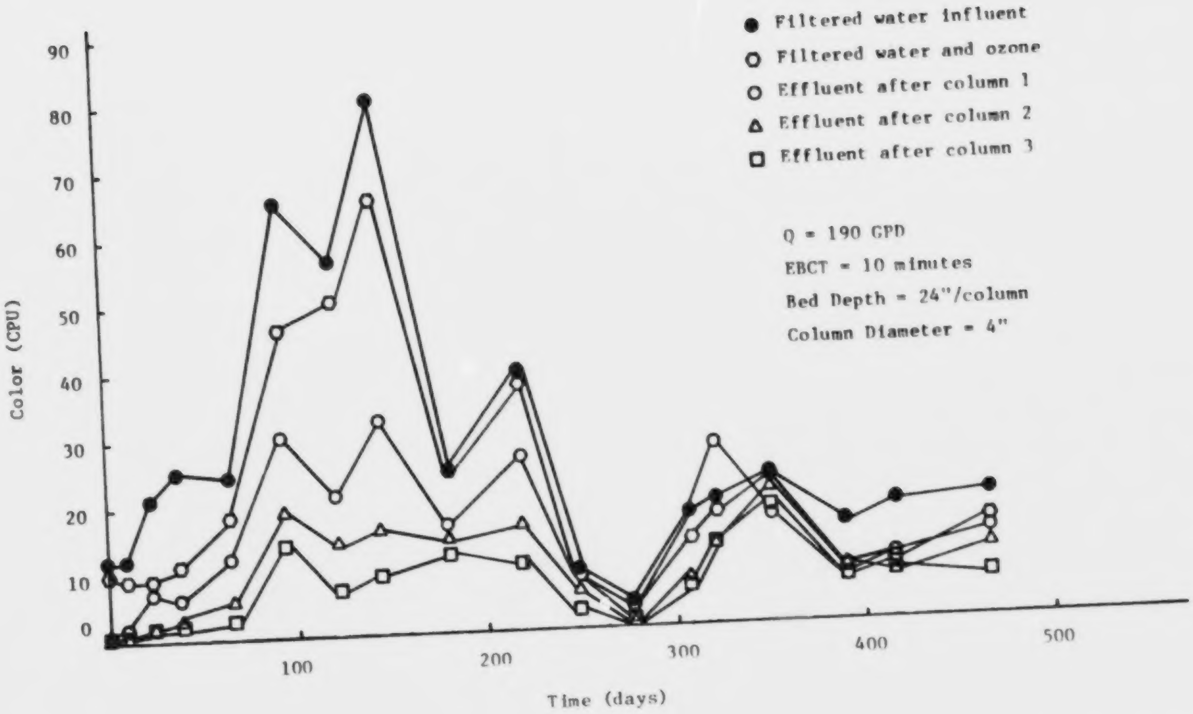


Figure 87. Influent and effluent color by columns for filtered water and ozone GAC system at Melbourne.

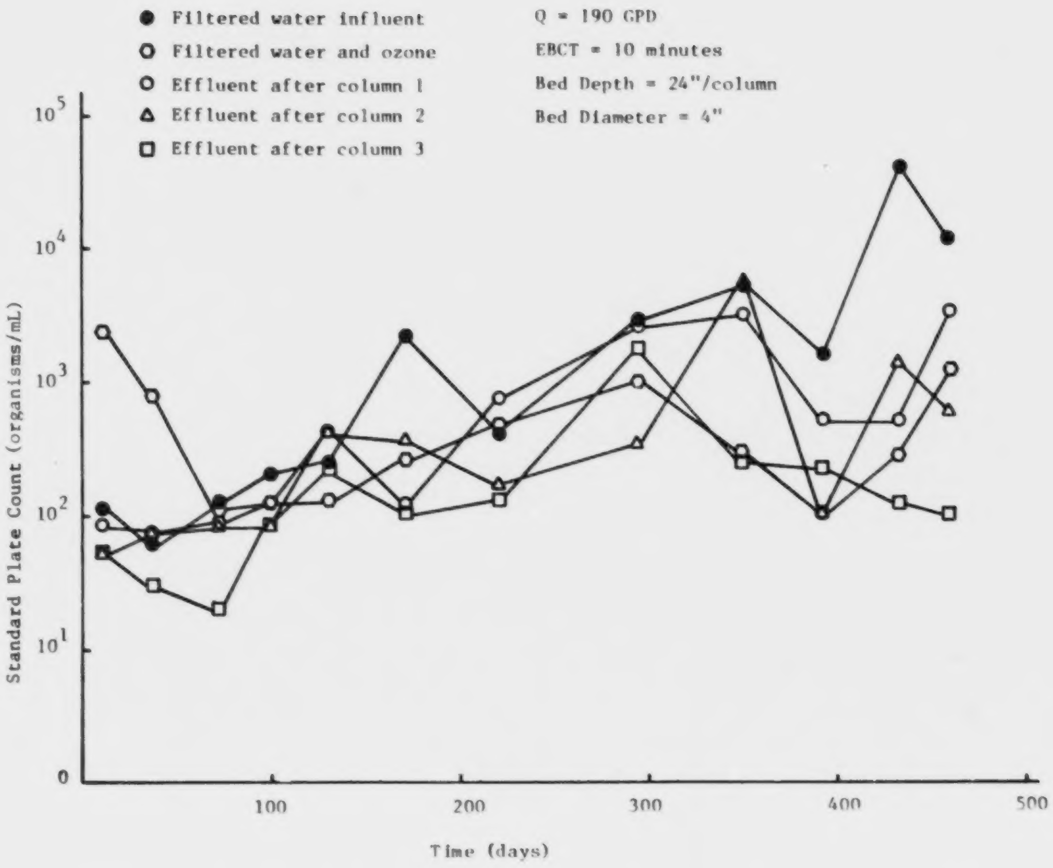


Figure 88. Influent and effluent standard plate count by columns for filtered water and ozone GAC system at Melbourne.

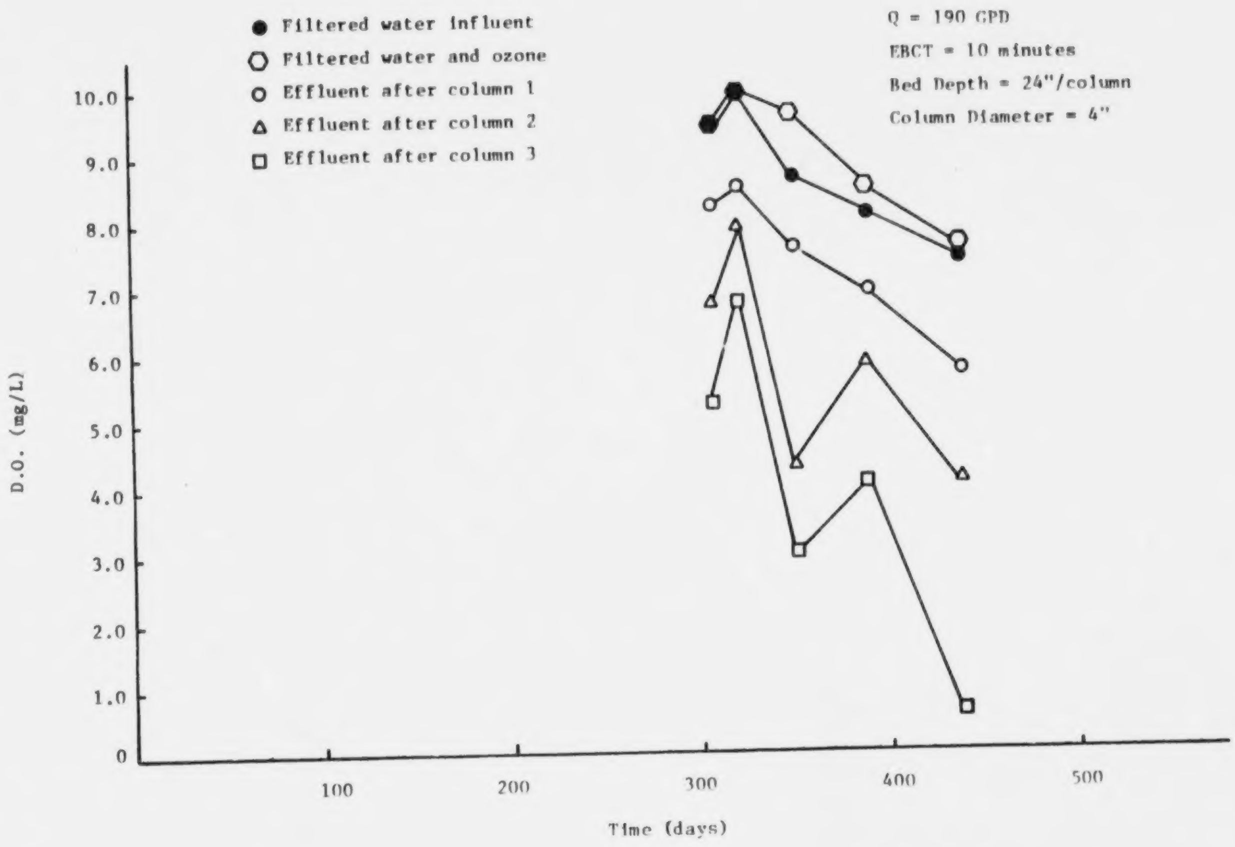


Figure 89. Influent and effluent dissolved oxygen by columns for the filtered water and ozone GAC system.

increased removal of 16% color, 10% TOC and 11% THMFP relative to the FW/GAC system. This was directly due to the ozone which alone removed 2.24 x 10^6 cpu of color, 0.22 x 10^6 mg TOC and 0.02 mg x 10^6 of THMFP. The removals in the ozone contactor more than accounted for the additional percentage of color, TOC and THMFP reduction in the FW/O_3/GAC system relative to the FW/GAC system. The GAC columns in the FW/O_3/GAC systems removed 3.77 x 10^6 cpu color, 1.15 x 10^6 mg TOC and 0.08 x 10^6 mg THMFP. Pretreatment by ozone reduced the capacity of the GAC to remove color by 28%, TOC by 7% and THMFP by 11%. Therefore ozonation prior to GAC increased the overall capacity of the FW/O_3/GAC system but reduced the ability of GAC to remove THMFP, TOC and color. This reduction could be caused by a chemical reaction with ozone that reduces the physical adsorbability of the organics. However, since ozone does improve overall removal but reduce the effectiveness of GAC, the most logical sequence of treatment would be ozonation preceded by GAC.

The SPC and DO for the FW/O_3/GAC system are shown in Figures 87 and 88. After day 300 the SPC and DO reductions are greater for GAC columns receiving ozonated water as compared to the GAC columns receiving unozonated water. The SPC, as with the FW/GAC system, decreased through each column, and increased with time due to changes in plant coagulation pH. SPC did not increase with time after alum coagulation was initiated on day 260. SPC did decrease through the columns at all times which again indicates that SPC is not a good measure of GAC biological activity although the SPC from the FW/O_3/GAC was higher than that from the FW/GAC. The SPC and DO data indicate greater biological activity in the FW/O_3/GAC system compared to the FW/GAC system. However the THMFP, TOC and color removals for the FW/O_3/GAC columns were respectively 28%, 7% and 11% less. This indicates that biological activity is not, but that physical adsorption is, a major mechanism of THMFP, TOC or color removal and that ozonation reduces the adsorbability of the THMFP, TOC or color producing molecules.

7.7.5 Chlorine Dioxide Filtered Water GAC

Chlorine dioxide, dosed at 1 mg/L as Cl, was used to pretreat the plant Melbourne finished water before GAC adsorption in a third system. The ClO_2 was applied in a reactor identical to the ozone contactor. The detention time was 30 minutes and there were six equally baffled chambers in the reactor. The influent and effluent THMFP, TOC and color concentrations for the

FW/ClO_2/GAC system are shown in Figures 90, 91, and 92. This system was only operated for 268 days because, relative to either the FW/GAC or the FW/O_3/GAC system, little if any improvement was noted. This system was discontinued at the time alum was beginning to be utilized so no data were collected for alum coagulated water in this system.

The ClO_2 alone did reduce the THMFP by 3.6% during operation. The total THMFP removal was 7,395 mg for a removal of 0.02 mg THMFP/mg ClO_2 for the conditions employed. This contactor also had some deposits, however, they were not nearly as numerous or dark as with the ozonator contactor. This observation indicated a $CaCO_3$ post-precipitate following plant treatment and little biological growth. Had this system received alum-treated water there likely may have been more deposits. The TOC removal in the ClO_2 contactor was 4.2%. The total TOC removal was 113,662 mg for a 0.15 mg TOC/mg ClO_2 removal ratio. The total percentage of color removal for the ClO_2 system was 7.2%. The total color removal was 425,108 cpu for a removal ratio of 1.10 cpu/mg ClO_2. The ClO_2 dose was kept at 2.0 mg/L because of Florida state limitations on ClO_2 use in a public water supply.

As shown in Figure 92 color removal is accomplished through the FW/ClO_2/GAC system by the addition of ClO_2 and each GAC column. Color as in all other GAC systems is removed more efficiently than either THMFP, 71% color removal versus 30% THMFP and 32% TOC removal for the operating period. The color standard of 15 cpu or less was met by this system for the first 95 days of operation far exceeding the 8 day operating period when the THM regulation of 0.10 mg/L was met. The GAC capacity for color removal to meet regulation in this system is 264 cpu/gm GAC. The GAC capacity for THMFP reduction to meet the THM regulation was 0.54 mg THMFP/gm GAC.

The total amounts of THMFP, TOC and color removed during operation of the FW/ClO_2/GAC system were 62,834 mg THMFP, 919,710 mg TOC and 4,248,019 cpu color. These removals were less than the FW/GAC system by 3.6% mg for THMFP removal, by 3.6% for TOC removal and by 0.3% cpu for color removal. This is because of ClO_2 pretreatment, since that was the only difference between the FW/GAC and the FW/ClO_2/GAC systems. As with O_3, pretreatment with ClO_2 reduced the efficiency of the GAC columns by 6.8% for THMFP removal, by 7.9% for TOC removal and by 7.6% for color removal. Although ClO_2, like O_3 alone, improved treatment, ClO_2 pretreatment was observed to be an overall

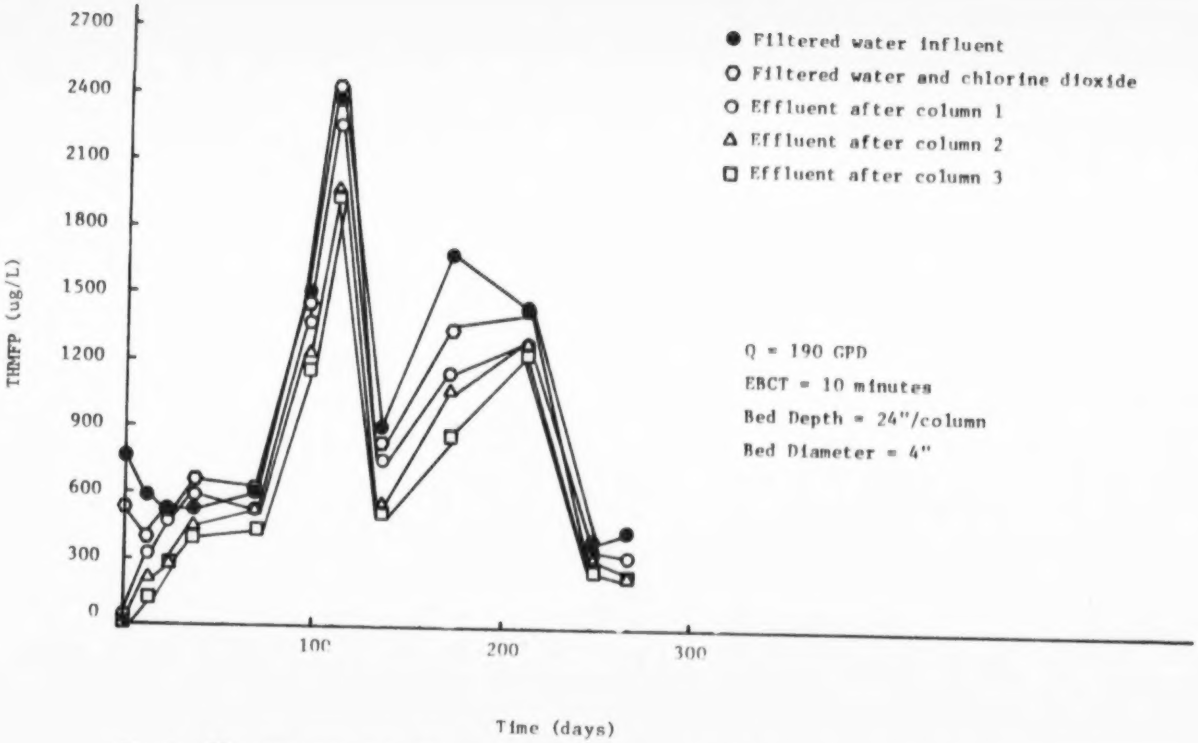


Figure 90. Influent and effluent THMFP by columns for filtered water and chlorine dioxide GAC system in Melbourne.

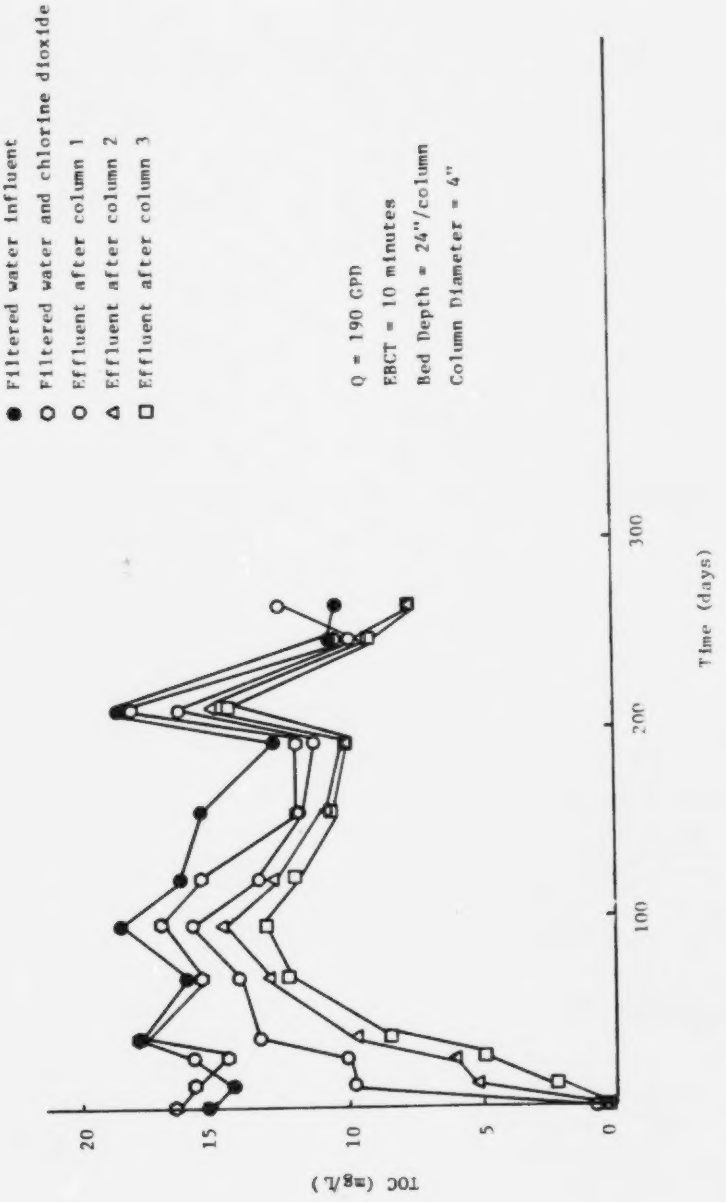


Figure 91. Influent and effluent TOC by columns by filtered water and chlorine dioxide GAC system at Melbourne.

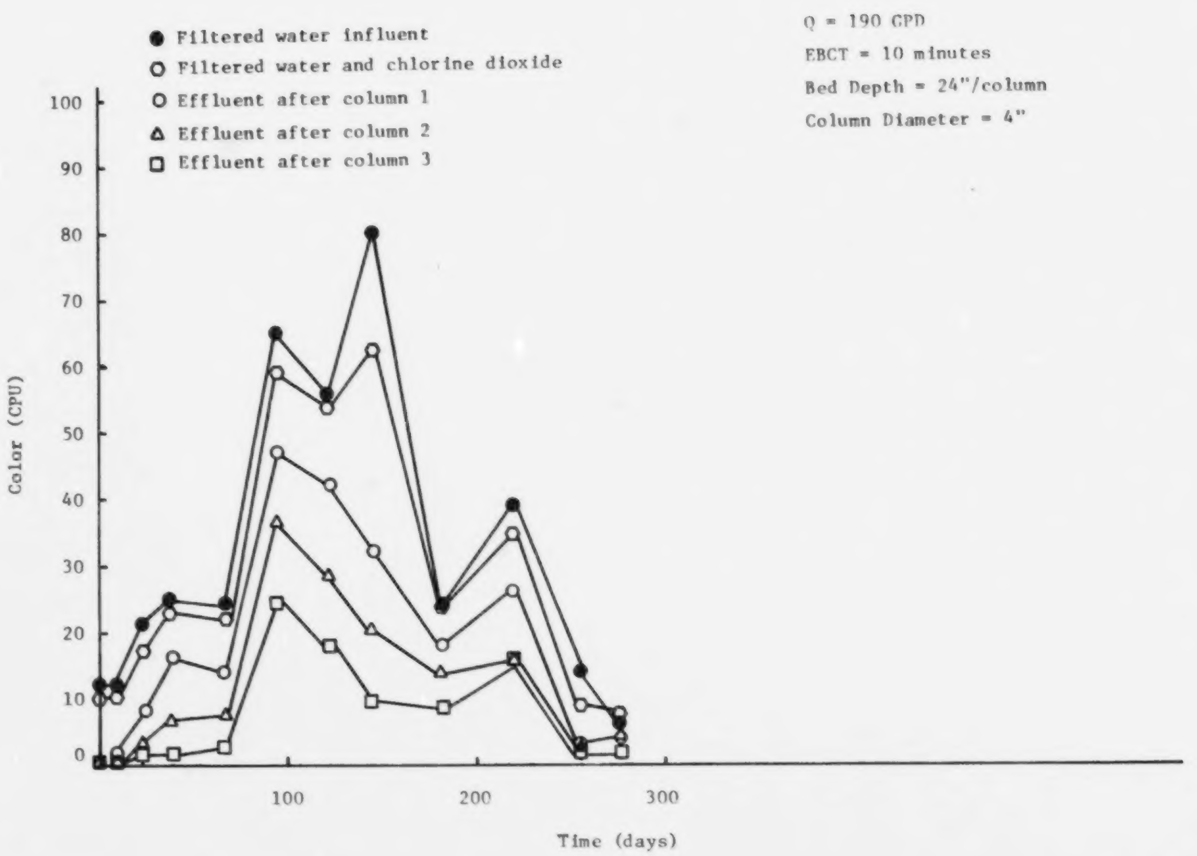


Figure 92. Influent and effluent color by columns for filtered water and chlorine dioxide GAC system at Melbourne.

disadvantage for THMFP, TOC and color removal by GAC adsorption. However as with ozone, ClO_2 oxidation may improve THMFP, TOC and color removal after GAC.

The influent and effluent SPC for each column and the ClO_2 contactor is presented in Figure 93. The ClO_2 did generally reduce the SPC and a general trend of increasing SPC with time due to process changes is observed. These data, as did the data for the FW/GAC and FW/O_3/GAC systems, show that SPC increased with time through the system and decreased through each column. The THMFP, TOC and color removal decreased (with time and after ClO_2 oxidation) which suggests physical adsorption instead of biological activity as the major mechanism of organic removal in these systems. Monitoring of DO did not begin until after the FW/ClO_2/GAC system was discontinued and therefore is not presented.

7.7.6 Raw Water GAC

The raw water granular activated carbon (RW/GAC) system received untreated Lake Washington water and operated for 268 days. The influent and effluent THMFP, TOC and color for each column in the RW/GAC system are shown in Figures 94, 95, and 96. This GAC system had the heaviest THMFP, TOC and color loadings of any of the GAC systems investigated. The average raw water THMFP concentration was 3030 ug/L with a standard deviation of 1536 ug/L. The average TOC concentration was 32 mg/L with a standard deviation of 2.4 mg/L. The average raw water color concentration was 167 cpu with a standard deviation of 42 cpu. The high raw water average TOC concentration and low standard deviation shows that Lake Washington water is consistently high in organic content. Although the THMFP and color are also seen to be large, their variability is because of their respective standard derivations. This variability is due to both the natural variation in quality and the variability associated with measurement.

The RW/GAC system produced an effluent through the system that was less than the 0.10 mg/L THM regulation for the first three days of operation. This 0.10 mg/L THM regulation was met in the effluent of only the third column, 76 ug/L, as the THMFP from the first and second columns were 186 ug/L and 111 ug/L respectively. The capacity for removal of THMFP was 0.48 mg THMFP/gm GAC. During this three-day period, the RW/GAC system removed 95% of the applied THMFP.

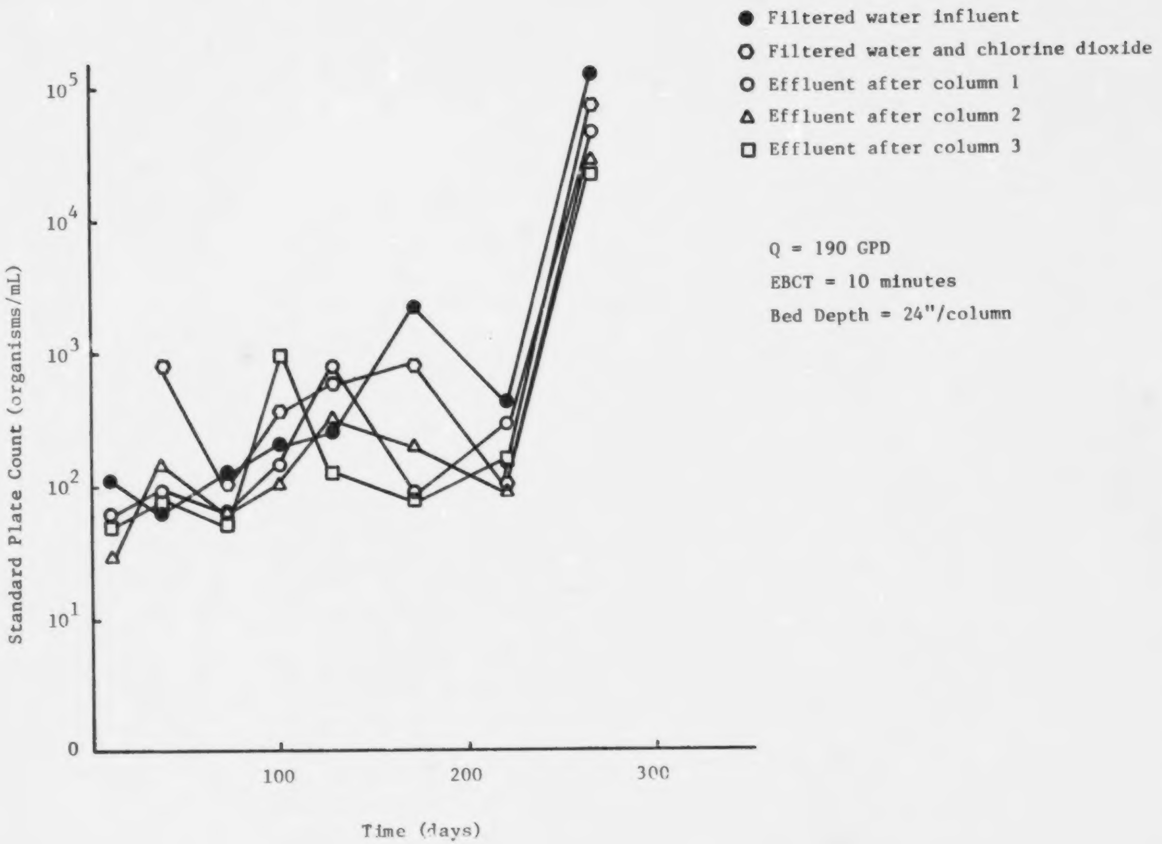


Figure 93. Influent and effluent standard plate count by columns for filtered water and chlorine dioxide GAC system at Melbourne.

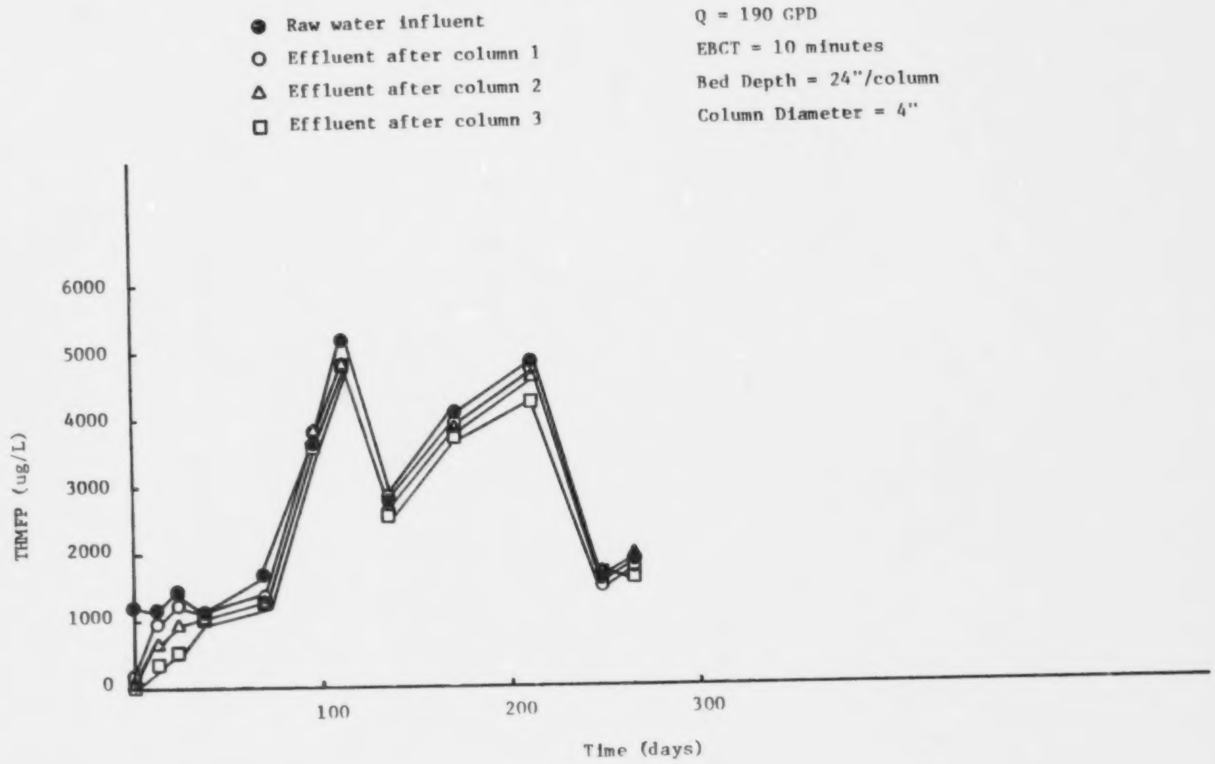


Figure 94. Influent and effluent THMFP by columns for raw water GAC system at Melbourne.

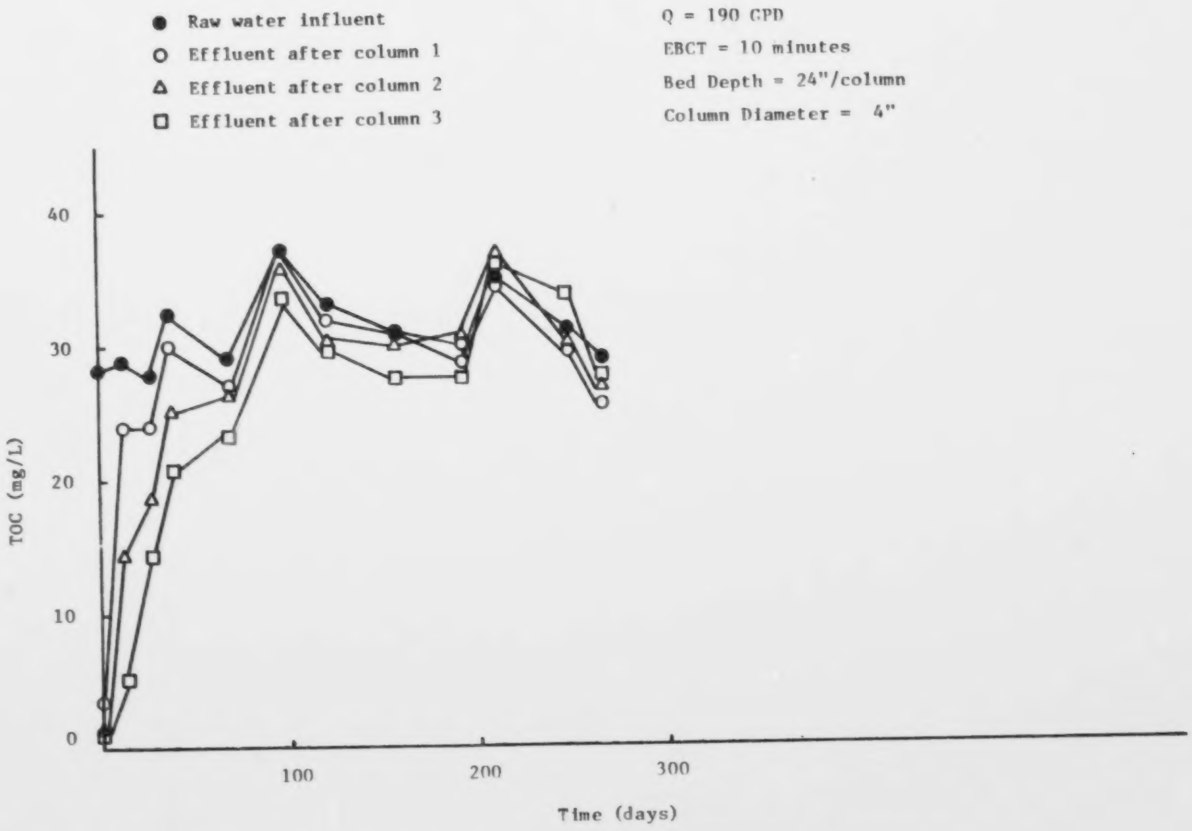


Figure 95. Influent and effluent TOC by columns for raw water GAC system at Melbourne.

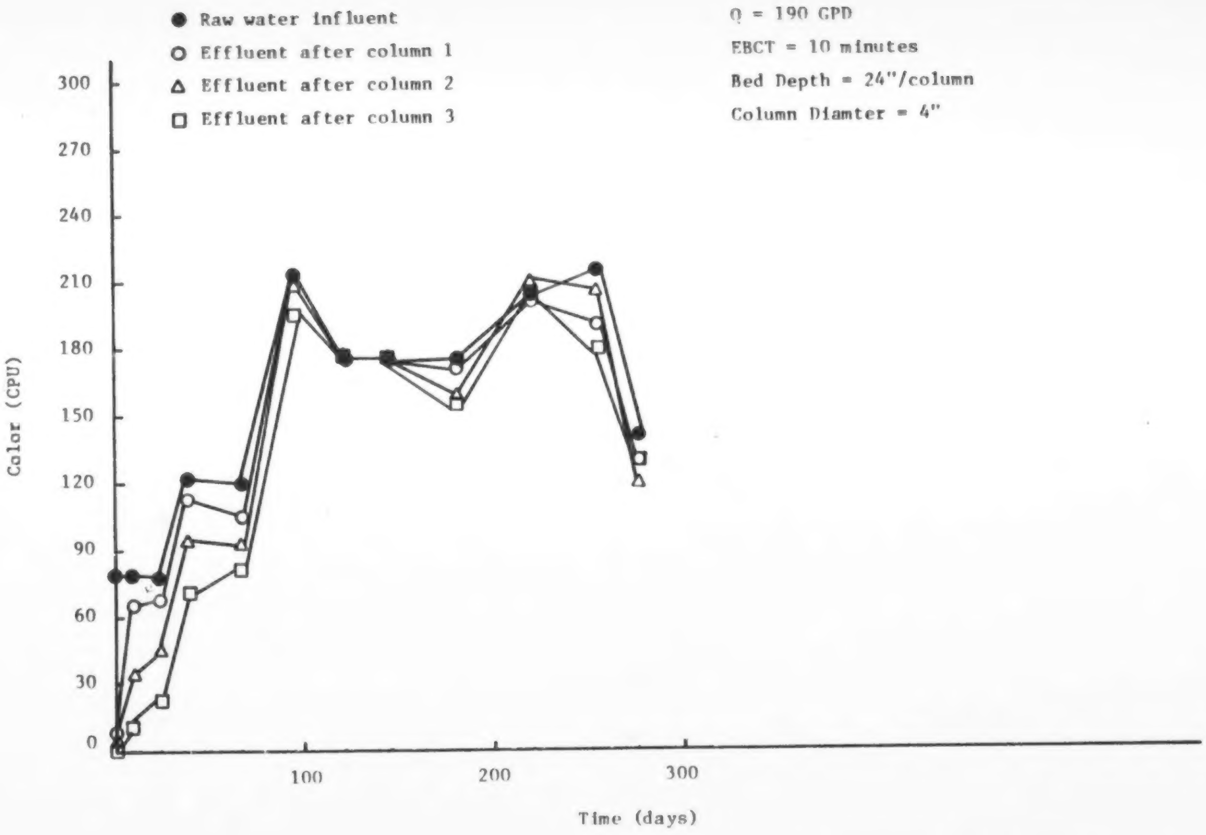


Figure 96. Influent and effluent color by columns for raw water GAC system at Melbourne.

The total THMFP, TOC and color removed by the RW/GAC system during the 268 days of operation were 86,689 mg THMFP; 945,197 mg TOC; and 4,076,502 cpu color. The RW/GAC was essentially exhausted after operating for 102 days for color removal, 211 days for TOC removal and 120 days for THMFP removal. The capacities of the RW/GAC system for meeting the THMFP and color standard were 0.48 mg/gm and 140 cpu/gm respectively. The same capacities to meet standards for the FW/GAC system were 0.56 mg/gm for THMFP removal and 240 cpu/gm for color removal, which represents a 17% increase in the GAC capacity for THMFP removal and a 71% increase in the GAC capacity for color removal. Consequently, the optimum placement of GAC columns in a water treatment plant would be after coagulation to maximize GAC life.

The influent and effluent SPC of the flows for each column is shown in Figure 97. The SPC of the raw water system is observed to increase slightly with time which increases SPC through the FW/GAC system with time although SPC generally decreases through the columns for each sample. The incremental percent removal and influent concentration of THMFP, TOC and color is plotted as a function of time in Figure 98. The percentage of removal of either TOC or color as shown in Figure 98 does not appear to increase as the concentration of TOC or color available to the columns increases. The percent THMFP removal dose appear to increase as the THMFP concentration of the influent increases. The large fluctuation in the raw water THMFP concentration is due, in part, to an increased chlorine does in the THMFP measurement technique after fifty days in order to maintain a residual through the 48 hour reaction period. The RW/GAC columns do not remove any more TOC after day 209 and appear to be exhausted at that point. The general trend is decreasing reduction of TOC, color or THMFP until exhaustion is reached without any continuing removal. These results indicate that biological activity is present but does not significantly increase the capacity of GAC for color, TOC or THMFP removal. If biological activity was significant, the opposite trend would have been expected. The tendency for decreasing removal indicates physical adsorption is the means by which color, TOC and THMFP are removed in these GAC systems. Placing the GAC systems after coagulation would seemingly remove the larger organic molecules prior to GAC adsorption and reduce GAC pore blockage, thereby enhancing GAC capacity.

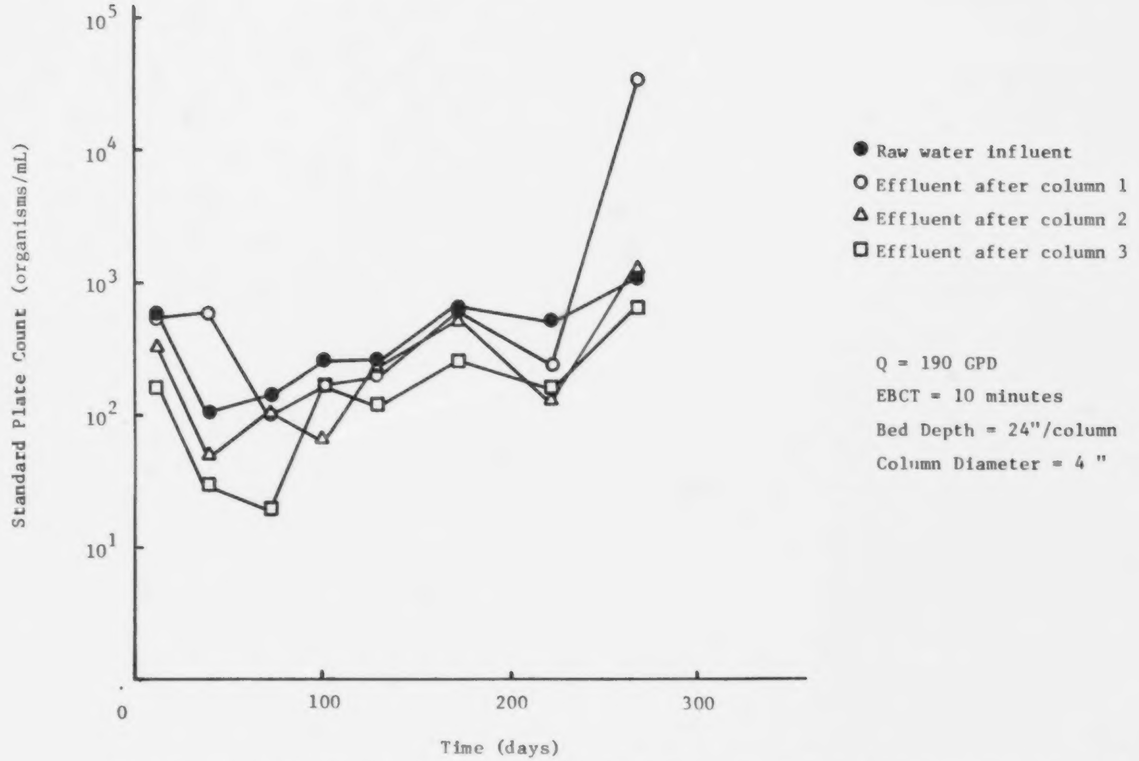


Figure 97. Influent and effluent standard plate count by columns for raw water GAC system at Melbourne.

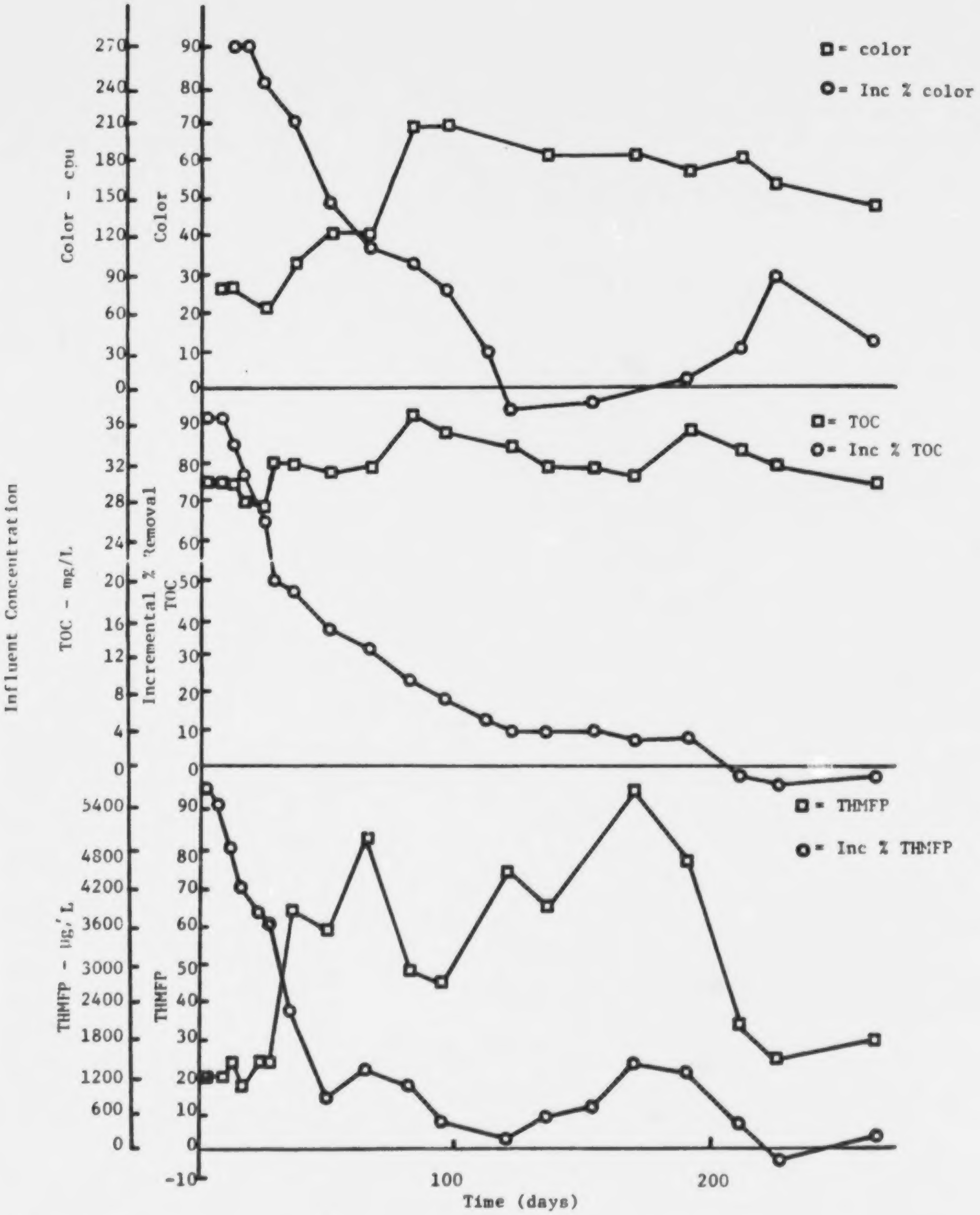


Figure 98. % Incremental Removal and Influent Quality for THMFP, TOC, and Color versus time for the Raw Water GAC System

7.7.7 GAC Comparisons

Two different granular activated carbons, a Calgon F-400 coal base and a West Vaco lignin base, were compared for THMFP, TOC and color removal. The columns used for this comparison became available when the RW/GAC and FW/ClO_2/GAC systems were discontinued. The influent to these systems was Melbourne finished water and they were operated for 140 days. These systems were identical to the FW/GAC system except that they received only alum-treated influent. The influent and effluent THMFP, TOC and color for each of the three columns in the coal-based GAC (denoted as GAC 1) system GAC are shown in Figures 99, 100 and 101. The influent and effluent THMFP, TOC and color for each of the three columns in the wood-based GAC (denoted as GAC 2) are shown in Figures 102, 103 and 104.

The coal-based GAC produced an effluent that met the 0.10 mg/L THM regulation through columns 1, 2 and 3 for 7, 42 and 59 days of operation. The THMFP from column 1 after 21 days of operation was 107 ug/L, indicating that a period of operation longer than seven days was possible. However, the capacities for mg of THMFP removal per gm GAC using the wood-base carbon were 1.27 mg/gm, 1.79 mg/gm and 0.87 mg/gm for columns 1, 2 and 3 at the point of exhaustion as defined by the 0.10 mg/L THM regulation. The wood-base GAC system capacity for THMFP removal to meet the THM regulation of 0.10 mg/L was 2.49 mg/gm. This represented a 98% removal of the THMFP applied to the system before breakthrough which had removed a total of 114,769 mg of THMFP at this point.

The wood-based GAC system produced an effluent that had a THMFP less than the 0.10 mg/L THM regulation for only three days and only through the third column. Columns 1 and 2 in the wood-based GAC system never produced an effluent with a THMFP less than 0.10 mg/L. The wood-based GAC capacity for THMFP removal at the 0.10 mg/L point of breakthrough was 0.13 mg/gm. The wood-based GAC system had removed a total of 813 mg of THMFP at the point of the 0.10 mg/L THMFP breakthrough. The capacity of the coal-based GAC was 19 times (1915%) greater than the capacity of the wood-based GAC carbon to reduce the THMFP of the alum-treated water to the 0.10 mg/L regulation. This difference may also be seen by comparing Figures 99 and 102.

The influent and effluent TOC concentrations for each column in the coal-based GAC system is shown in Figure 100. There is no TOC standard;

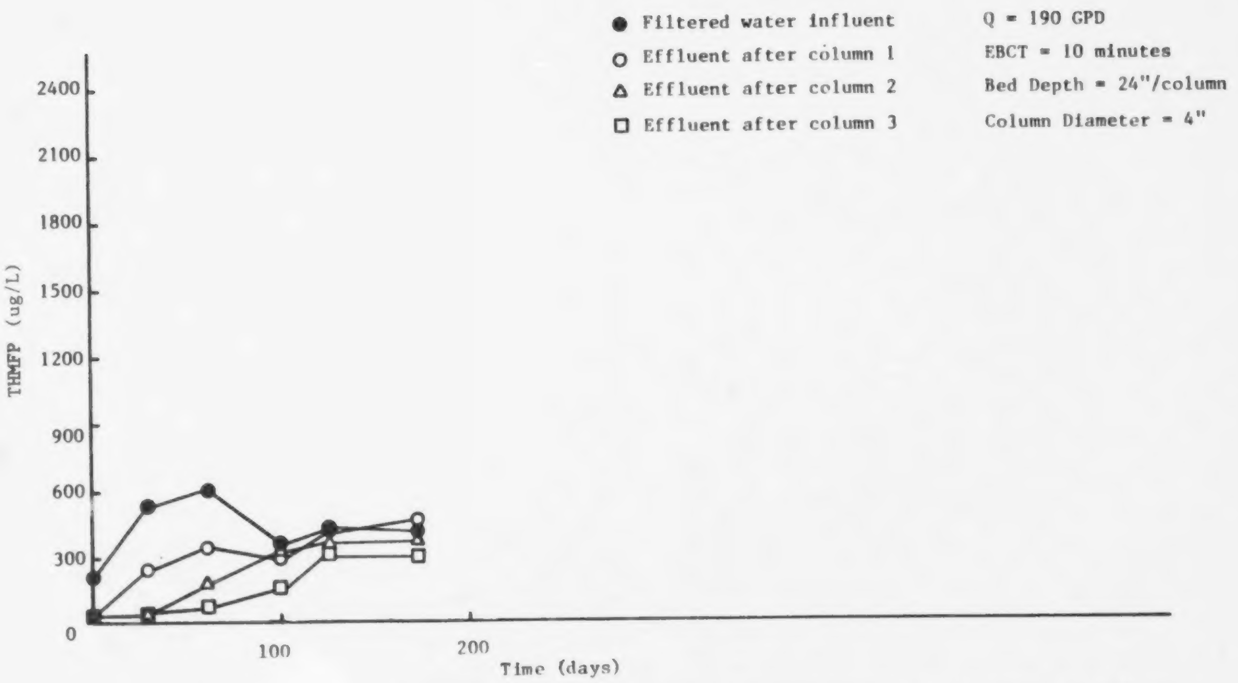


Figure 99. Influent and effluent THMFP by columns for filtered water GAC (1) system at Melbourne.

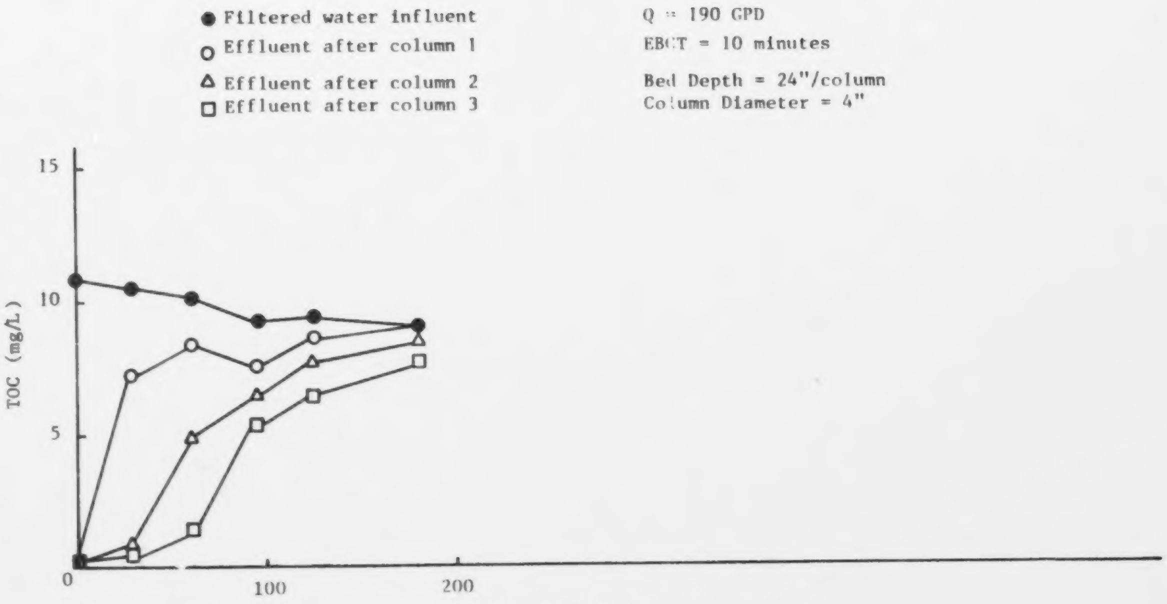


Figure 10D. Influent and effluent TOC by columns for filtered water GAC (1) system at Melbourne.

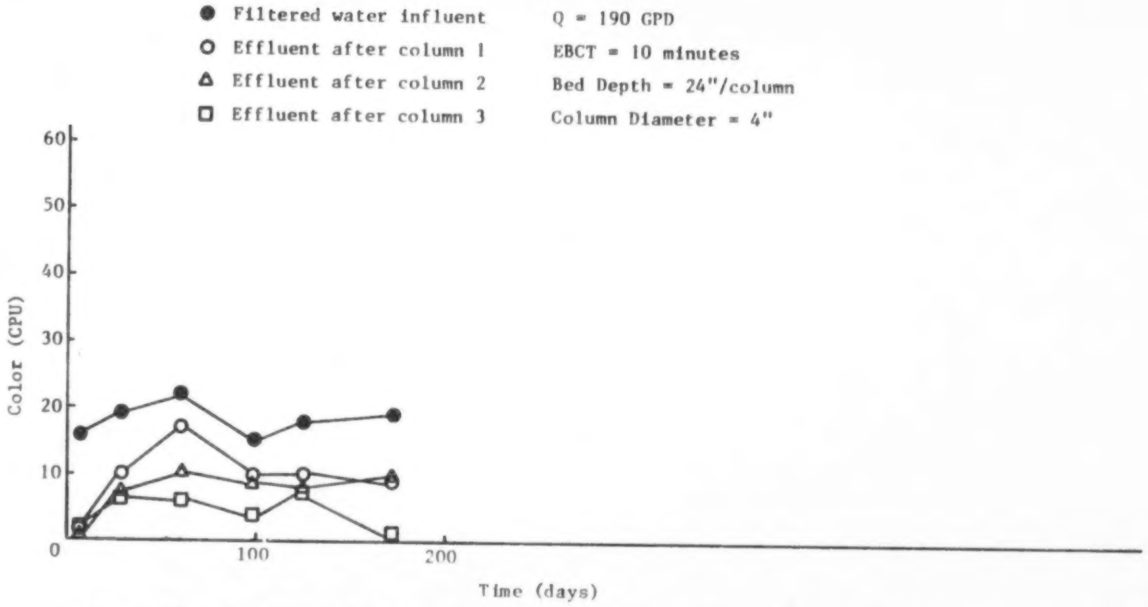


Figure 101. Influent and effluent color by columns for filtered water GAC (1) system at Melbourne.

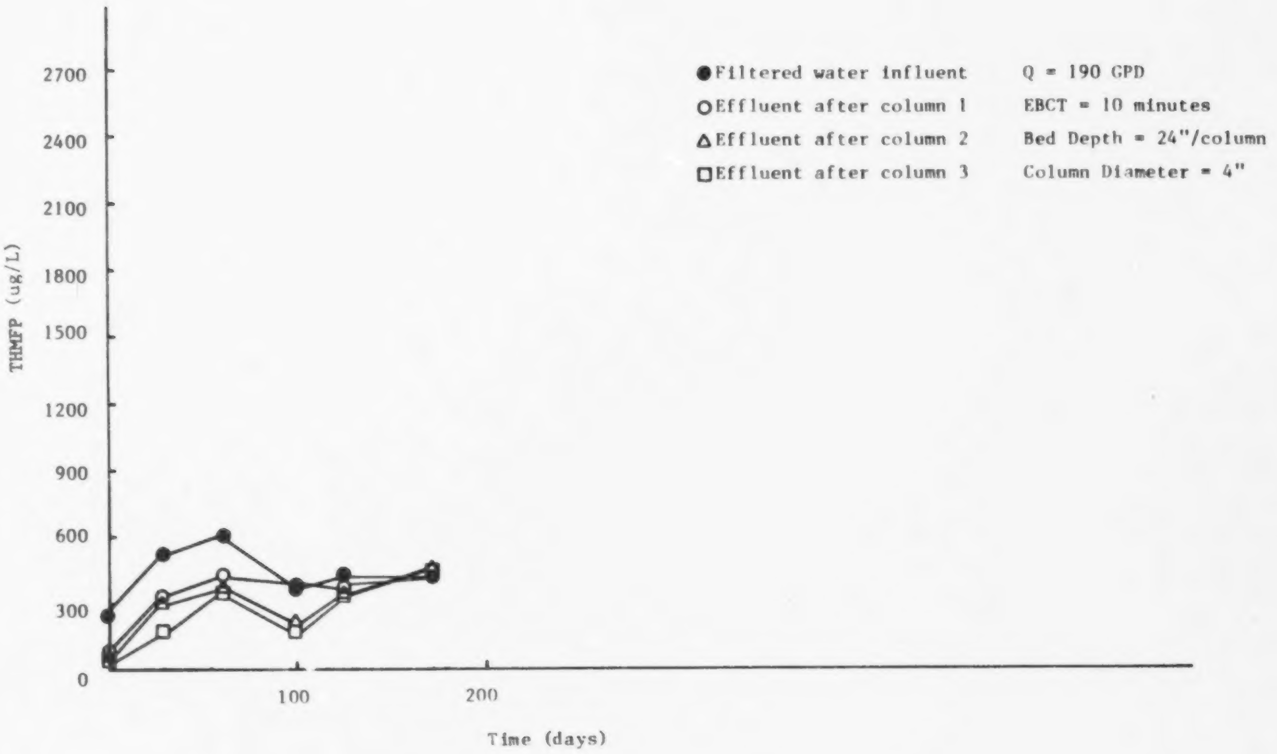


Figure 102. Influent and effluent THMFP by columns for filtered water GAC (2) system at Melbourne.

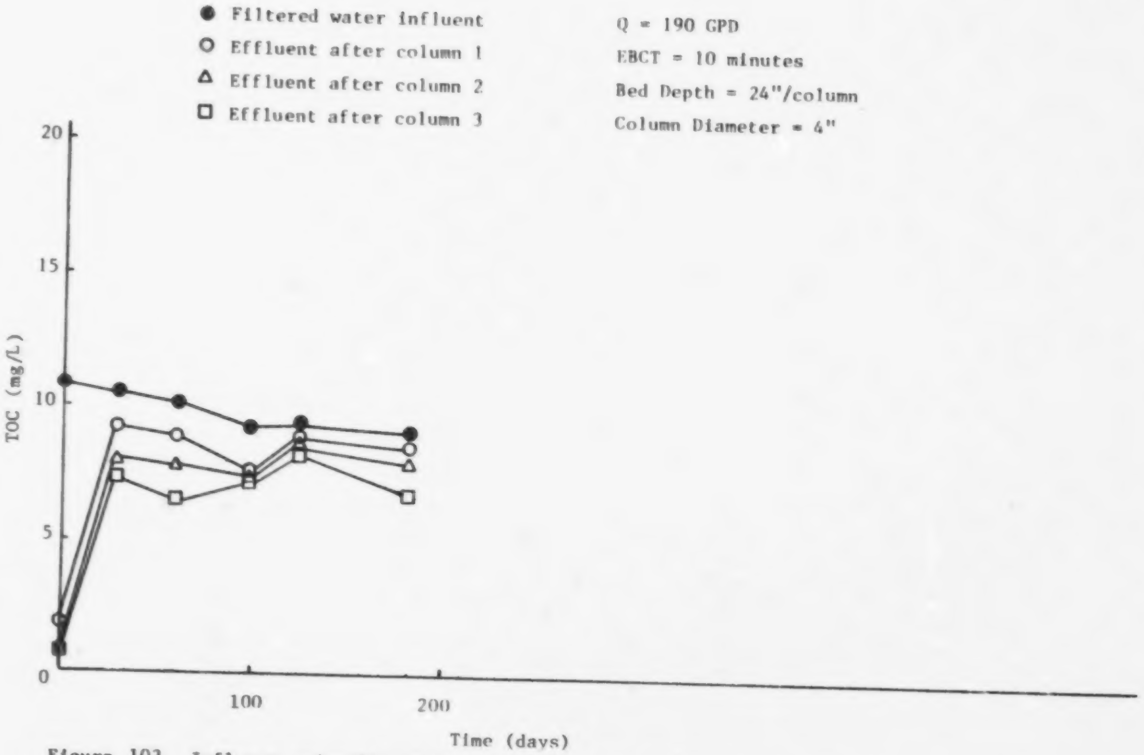


Figure 103. Influent and effluent TOC by columns for filtered water GAC (2) system at Melbourne.

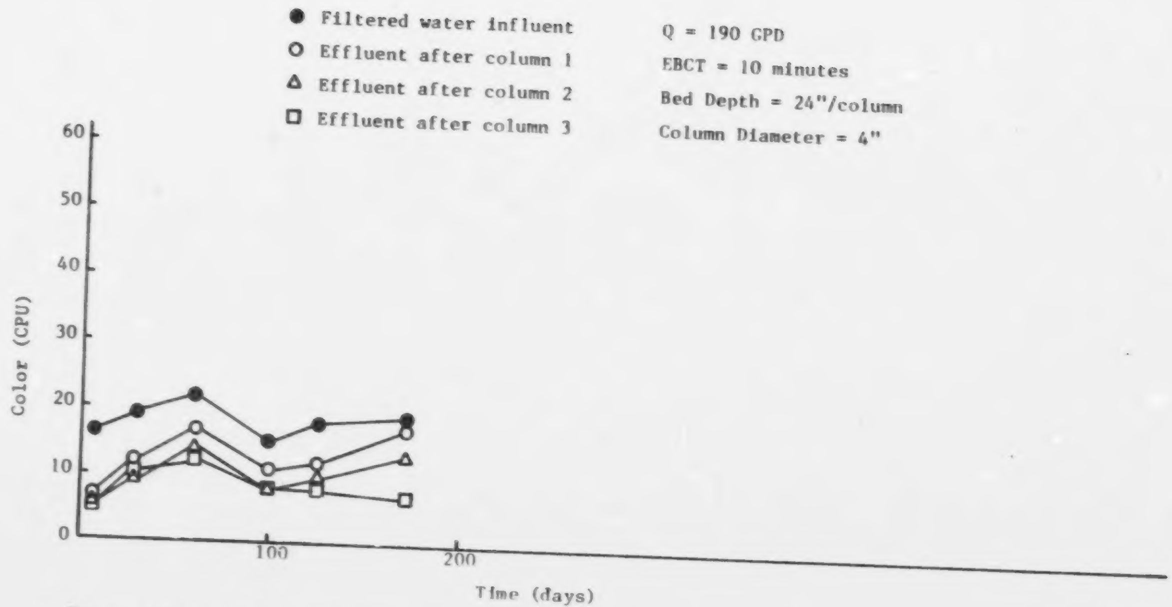


Figure 104. Influent and effluent color by columns for filtered water GAC (2) system at Melbourne.

however, for the 140 days of operation, the coal-based GAC removed 743,482 mg of TOC for a capacity of 125 mg TOC/gm GAC. The last increment of TOC removal was 35%, which did not vary more than 2% for the last 84 days of operation. The coal-based GAC capacity to remove 90% of the TOC in column 1 was 71.5 mg TOC/gm GAC. This was increased to 82.6 mg TOC/gm GAC for the 3-column system. These capacities appear to be reasonable estimates for 90% TOC removal from an alum-treated finished water by the coal-based GAC. The wood-based GAC did not reduce TOC as effectively as the coal-based GAC, as shown in Figure 103. The wood-based GAC system removed 368,090 mg of TOC or 29.2% of the applied TOC during the 181 day period of operation. The last increment of TOC removal was 13%. There was no period of 90% TOC removal as the first measurement made after three days of operation yielded 88% removal. The capacity of the wood-based GAC for TOC removal after 181 days was 62 mg/gm. The capacity of the coal-based GAC was twice that at the conclusion of the operating period.

The color removal through each column in the coal-based GAC system is shown in Figure 101. This effluent from this system never produced a color that exceeded the 15 cpu color standard. However, after 181 days of operation, 1,491,517 cpu of color had been removed for a coal-based GAC capacity of 252 cpu/gm. The percentages of incremental color removal for the first increment after three days and last increment after 181 days of operation were 74% and 71% respectively. The first cpu color standard was exceeded only through column 1 in the coal-based GAC system after 42 days. The GAC capacity for color removal was 116 cpu/gm at that point, which is far less than the system capacity which was never exceeded for the standard. The influent color varied from 12 cpu to 24 cpu for these studies but was usually above the 15 cpu standard.

The wood-based GAC color removal is shown in Figure 104. Although the removal of color by the wood-based GAC is not as great as the coal-based GAC, the effluent from wood-based GAC system also never exceeded 15 cpu color standard. The wood-based GAC system removed a total of 1,098,502 cpu of color during 181 days of operation for a capacity of 185 cpu/gm. This capacity and mass removals are 36% less than the coal-based GAC capacity and mass removal over the same period. The 15 cpu color standard was exceeded in columns 1 and 2 after 42 days of operation, giving capacities of 83 cpu/gm and 34 cpu/gm respectively.

As demonstrated by the preceding discussion, the coal-based GAC is significantly better for color, TOC and THMFP removal than the wood-based GAC for alum-treated Lake Washington water. The effect of pretreatment at Melbourne can be discussed since the same coal-based GAC was also used at the beginning of the 473-day study. The coal-based GAC carbon receiving alum-treated water had a capacity of 252 cpu/gm after removing 67.6% of the 2,205,273 cpu of color input to the system. Breakthrough of the 15 cpu color standard was never reached. The capacity of the coal-based GAC receiving alum-treated water to meet the 0.10 mg/L THM regulation was 2.49 mg/gm. The capacities of the coal-based GAC used in the FW/GAC system to meet the 15 cpu and 0.10 mg/L THM regulation were 240 cpu/gm for color and 0.56 mg/gm for THMFP. There is only a 4% improvement in the capacity for color removal but an 80% improvement in THMFP capacity using alum-treated effluent. This indicates optimizing pretreatment to GAC at Melbourne will produce a fivefold increase in GAC capacity.

The influent and effluent SPC and the DO for each column in the GAC systems utilizing the coal-based and wood-based GACs are shown in Figures 105, 106, 107 and 108. These Figures show that SPC was high and variable and that DO decreased across each column. There is no significant difference between SPC counts and DO reductions in either system, yet there were major differences in color, TOC and THMFP removals. As before, the results indicate biological activity is not a significant factor in the removal of color, TOC or THMFP but that their removal is dependent on physical adsorption and type of GAC utilized.

7.7.8 GAC Summary

The capacities of the different GAC systems to meet the THM regulation and color standard of 0.10 mg/L and 15 cpu are shown in Table 56. As can be seen in Table 56, the FW/O_3/GAC system has the highest capacity for either color or THMFP removal. The improvement in THMFP and color removal in this system resulted from the use of ozone which removed an additional 11% THMFP, 10% TOC and 16% color relative to the FW/GAC system.

The type of GAC selected and the optimization of pretreatment are important considerations for optimizing removal of color and THMFP. The coal-based carbon was seen to have 37% more capacity for color removal and almost twentyfold more capacity for THMFP removal to meet the THM regulation or the color

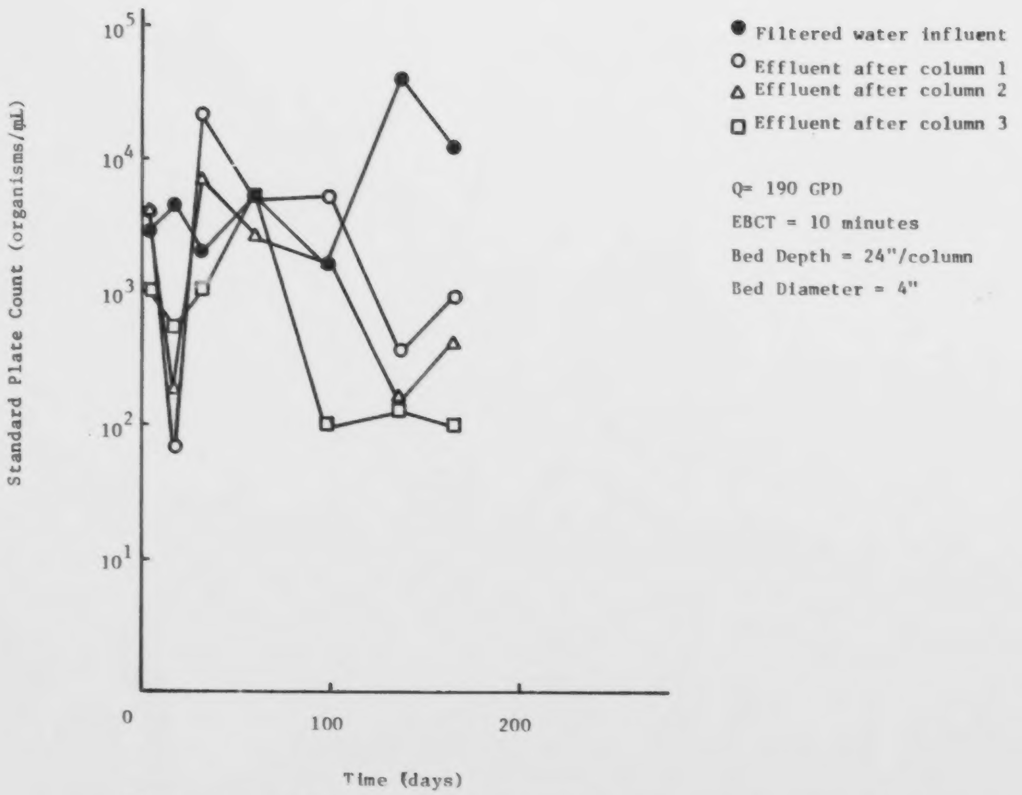


Figure 105. Influent and effluent standard plate count by column for filtered water (1) system at Melbourne.

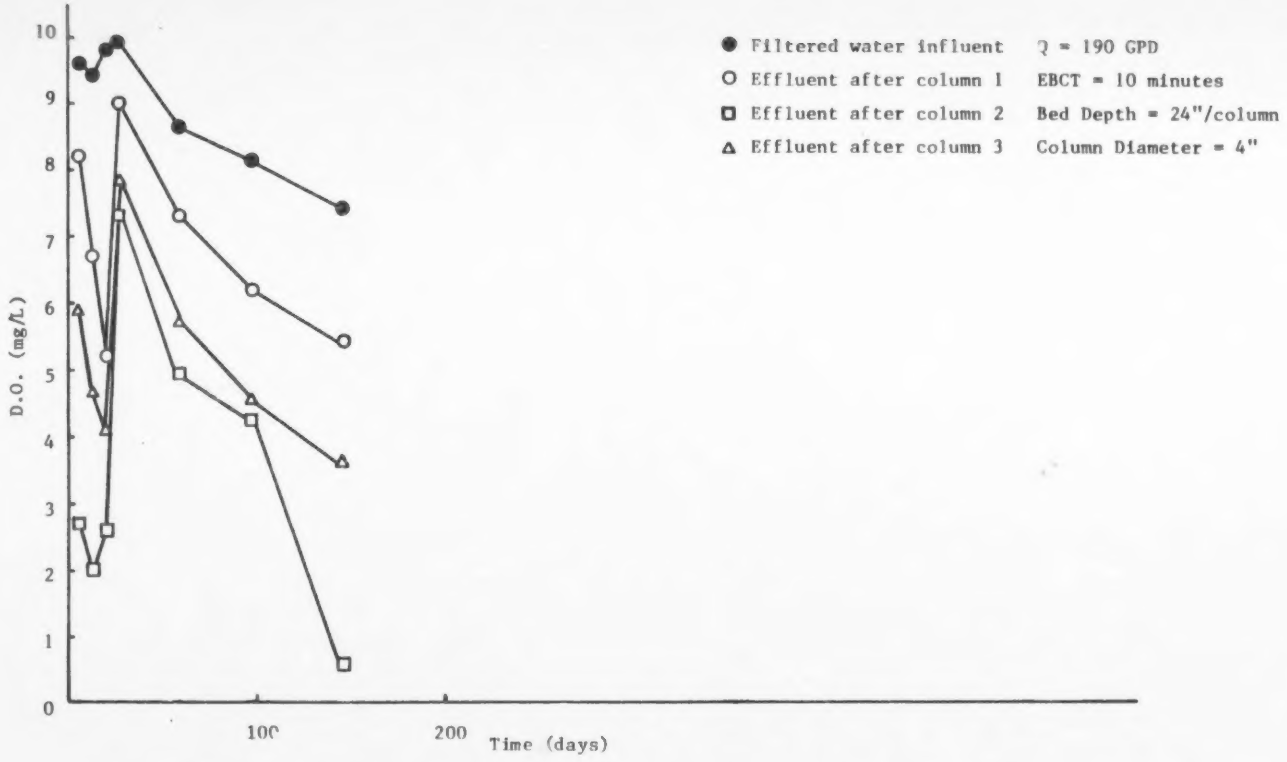


Figure 106. Influent and effluent dissolved oxygen by columns for filtered water GAC (1) system at Melbourne.

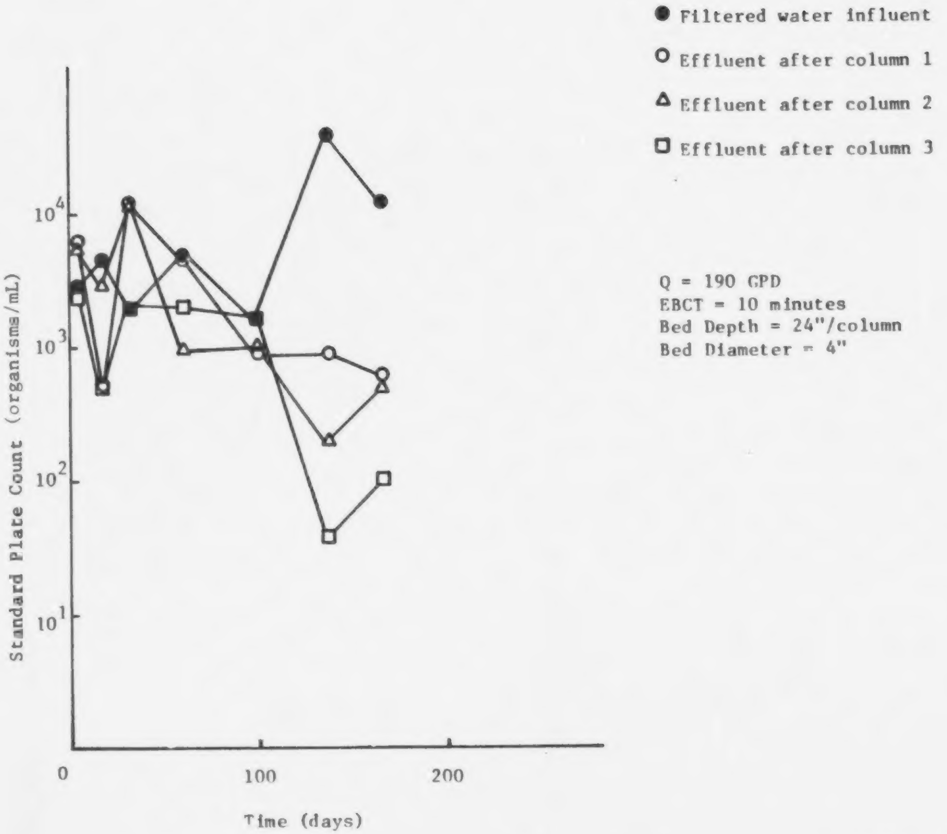


Figure 107. Influent and effluent standard plate count by columns for filtered water GAC (2) system at Melbourne.

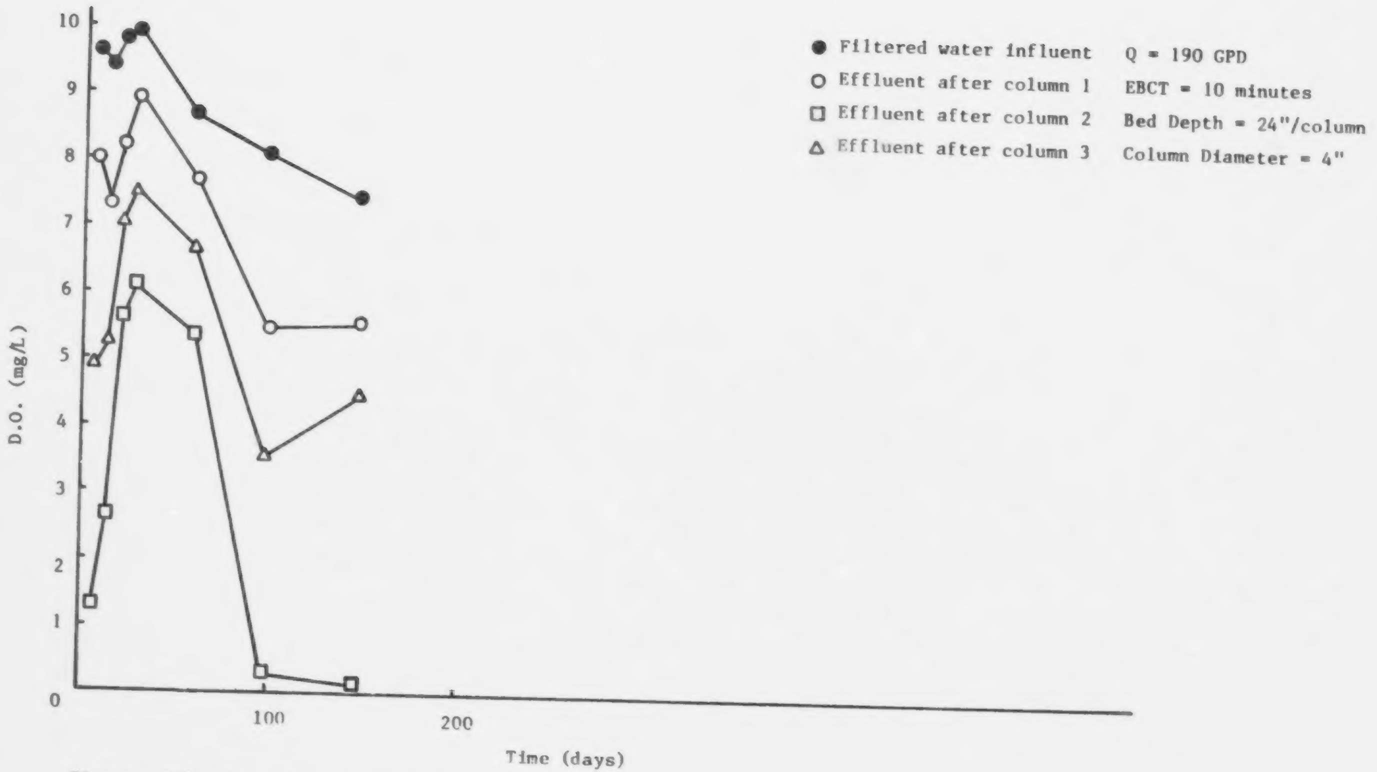


Figure 108. Influent and effluent dissolved oxygen by columns for filtered water GAC (2) system at Melbourne.

Table 56. GAC Capacities to Meet Color Standard and THMFP Regulation Under Melbourne Test Conditions

Systems	Capacities to Meet Standards or Regulation	
	15 cpu color cpu/gm	0.10 mg/L THM mg/gm
FW/GAC	240	0.56
FW/O_3/GAC	265	1.04
FW/ClO_2/GAC	264	0.54
RW/GAC	140	0.48
FW/GAC - coal base	252*	2.49
FW/GAC - wood base	185*	0.13

*Minimum capacity, breakthrough never reached.

standard. When coagulation was optimized, the capacity of the coal-based carbon was observed to increase 4.5 times. These factors, GAC type and pretreatment, could potentially enhance the life of the GAC system ninetyfold in Melbourne.

Because of the need to optimize pretreatment, the RW/GAC was observed to have the lowest capacity for THMFP, TOC or color removal. Relative to the FW/GAC system, the RW/GAC capacity to meet the 0.1 mg/L THM regulation and 15 cpu color standard was 17% less for THMFP and 71% less for color reduction. This system, RW/GAC, had the lowest capacities of any system investigated, seemingly indicating the need for the removal of large molecules that may block the GAC pores preventing further adsorption.

The general shapes of the THMFP, TOC and color curves showing influent and effluent concentrations for each column were similar. There was an initial period of rapid breakthrough during the first 11 to 56 days of operation, depending on the parameter. This period was followed by periods of less rapid breakthrough with continuing removal usually occurring, although some systems (RW/GAC, FW/GAC for THMFP removal) appeared to reach saturation. The incremental percentage of removals typically would slowly decrease with time. As the capacity of the GAC was slowly utilized decreasing the incremental percent removal, the SPC increase and the DO reduction across each GAC column indicated biological activity. So the trend of increasing biological activity, as indicated by increasing oxygen consumption was accompanied by a decrease in incremental percentage of removal. This was observed in every GAC system and indicates that biological activity is not a significant means of THMFP, TOC or color removal in these GAC systems. The decreasing incremental percentage of removal as time increased suggests that physical adsorption of a mixture of organics, some strongly and some weakly adsorbed, was the means of organic removal by GAC at Melbourne.

Of all the parameters measured--THMFP, TOC and color--in each GAC system, color was removed most efficiently by GAC. The percentage of removal of color was generally twice as much as for either THMFP or TOC. The percentage of removal of TOC was generally equivalent to the percentage of THMFP reduction.

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APPENDIX A.1

Distribution Tables

MELBOURNE DISTRIBUTION SYSTEM

Table A-1. Electronics Drive and Wickham Road, 7.6 miles from the South Melbourne Water Treatment Plant. Site No. 1.

DATE	Temp °F	pH	Color cpu pH[1]	Color cpu pH[2]	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
01/05/83	68.0	8.35	1	1	4.60		-1			
01/12/83	66.0	8.65	2		3.60		-1			
01/19/83	60.0				3.60		-1			
02/02/83	67.0	8.70	11	9	3.80	470	-1			
02/15/83	64.0									
02/16/83	64.0	8.30	6	21	3.80	10	-1			
03/02/83	64.0	8.70	13	21	3.60	20	-1			
03/16/83	68.5	8.60	7	21	2.80	140	-1			
03/30/83	67.0	8.75	2	8	4.00	50	-1			
04/13/83	73.5	9.00	3		3.80		-1			
04/14/83	73.5	9.00	3		4.00		-1			
05/05/83	78.5	8.65	1		4.20		-1			
05/23/83	80.0	8.90	4	18	4.60	4	-1			
05/05/83	82.0	8.05	2	19	5.20	1	-1			
06/21/83	83.0	8.10	8	20	6.20	<1	-1			
05/29/83	85.5	8.90	2				-1			
07/06/83	84.5	8.35	2	8	0.75	60	-1			
07/18/83	89.0	8.65	14	16	2.20	30	-1			

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

MELBOURNE DISTRIBUTION SYSTEM

Table A-2. John Rodes Boulevard and Rogers Place, northwest corner, 8.7 miles from the South Melbourne Water Treatment Plant. Site No. 2.

DATE	Temp °F	pH	Color cpu pH[1]	Color cpu pH[2]	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
02/28-83	64.5	8.55	4	27	2.8	4	-1			
03/14/83	63.5	7.90	8	21	3.2	3	-1			
03/23/83	68.5	8.50	2	8	1.8	20	-1			
04/04/83	70.0	8.05	3		2.6		-1			
04/14/83	73.5				3.8		-1			
04/25/83	72.5	7.55	2		3.2		-1			
05/09/83	77.5	8.45	2		1.6		-1			
05/19/83	80.5				3.4		-1			12.1
05/23/83	81.5	8.70	2	15	4.2	2	-1			
06/06/83	84.0	8.05	2	16	3.8	2	-1		433	10.6
06/20/83	83.0	8.55	2	13	4.8	<1	-1	1.3		
06/27/83	84.5	8.40	3				-1			
07/06/83	86.5	8.50	2	12	4.4	2	-1	0.9		
07/15/83	85.0	7.90	13							
07/18/83	89.0	8.65	16	20	1.8	32	-1	0.8		
07/26/83	87.0	8.45	8				-1			8.7

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

MELBOURNE DISTRIBUTION SYSTEM

Table A-3. Pineapple Park, 11.1 miles from the South Melbourne Water Treatment Plant. Site No. 3.

DATE	Temp °F	pH	Color cpu pH^1	pH^2	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
04/20/82	81.0	7.75	35		0.2	137	-1	4.5		
04/27/82	78.0	7.65	11		0.2	150	-1	1.6		
05/04/82	76.0	7.70	21		0.2	83	-1	2.6		
05/11/82	81.0	7.90	7		0.2	277	-1	2.2		
05/18/82	80.5	7.70			0.1	98	-1			
05/25/82	82.5	7.65	7		0.1	206	-1	1.8		
06/01/82	86.0	7.55			0.1	47	-1			
06/08/82	86.0	7.55			<0.1	160	-1			
06/15/82	83.0	7.80	35		0.1	114	-1	5.7		
06/22/82	84.5	7.70	13		0.1	194	-1	4.2		
06/29/82	85.0	7.65	31		0.1	23000	-1 H	3.4		
07/07/82	84.5	8.10	45		<0.1	10100	-1 M	8.1		
07/13/82	85.0	7.10	45		<0.1	12450	-1	5.1		
07/20/82	82.0	7.20	27		0.1	20000	-1 M	3.1		
07/27/82	85.5	7.30	32		<0.1	155000	-1	3.4		
08/02/82	83.0	7.55	26		<0.1	12000	-1	2.6		
08/10/82	85.0	7.40	16		0.1	27000	-1 H	1.7		
08/17/82	82.0	7.20	16		0.1	17500	-1 M	2.8		
08/25/82	89.0	7.85	16		0.2	4500	-1	2.2		
09/07/82		7.60	65		<0.1	23600	-1	7.9		
09/14/82	90.0	7.55	2		<0.1	2500	-1	4.3		
09/21/82	83.5	8.20	4		<0.1	220	-1	1.0		
09/28/82	83.5	8.20	7		0.1	20	-1 M	1.7		
10/05/82	81.0	8.30	4		0.1	40	-1	1.0		
10/12/82	83.0	7.90	4		<0.1	6900	-1	1.1		
10/19/82	74.5	8.15	6		0.1	100	-1	0.3		
10/26/82	79.0	8.00	4		0.0	1050	-1	0.7		
11/02/82	74.0	7.00	4		<0.1	270	-1	0.9		
11/09/82	68.5	8.10	6		0.4	10	-1	5.3		
11/16/82	70.0	8.20	1		<0.1	200	-1	0.5		
11/22/82	77.0	7.60	4		0.1	28900	-1	0.4		
12/07/82	75.0	8.30			0.2	940	-1			
12/14/82	73.0	8.35	2		0.3	540	-1			
12/27/82	72.5	7.60			0.7	840	-1			
01/04/82	73.0	8.00	3		1.3	22	-1			
01/11/83	71.0	8.25	4		2.6	1	-1			
01/19/83					1.3	3	-1			
01/25/83	66.0	8.65	7		1.6	10	-1			
02/09/82	66.0	8.75	1		0.9	60	-1			

(continued)

MELBOURNE DISTRIBUTION SYSTEM (continued)

Table A-3. Pineapple Park, 11.1 miles from the South Melbourne Water Treatment Plant. Site No. 3.

DATE	Temp °F	pH	Color cpu		Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
			pH[1]	pH[2]						
02/23/83	66.5	8.55	3		0.4	540	-1 M			
03/09/83	71.0	8.15	9		<0.1	40	-1			
03/23/83	70.5	8.70	3		0.3		-1			
04/06/83	73.5	8.55	3		0.4		-1			
04/27/83	76.5	8.40	2		0.2		-1			13.67
05/10/83	78.0	8.20	2		0.1		-1 M			
05/25/83	85.0	8.40	4				-1			
06/06/83	82.0	7.85	3	15	1.4	2				
06/07/83	82.0	7.85	3				-1			
06/15/83	84.5	8.20	3				-1			
06/21/83	83.0	8.15	11	36	0.3	1	-1	3.4		
06/22/83	83.0	8.10	3				-1			
07/06/83	90.5	8.25	9	10	0.9	1	-1	3.8		
07/14/83	85.0	8.40		12			-1 M			
07/18/83	89.0	8.60	18	23	1.6		-1	2.3		
07/22/83	90.5	8.35	16				-1			

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

MELBOURNE DISTRIBUTION SYSTEM

Table A-4. Banberry Lane and Post Road, northwest corner, 11.3 miles from the South Melbourne Water Treatment Plant. Site No. 4.

DATE	Temp °F	pH	Color cpu pH[1]	Color cpu pH[2]	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
04/20/82	80.0	8.10	5		0.3	1	-1	0.8		
04/27/82	75.5	7.75	4		0.8	20	-1	0.6		
05/04/82	76.0	8.20	8		0.1	16	-1	1.0		
05/11/82	78.0	8.00			0.1	193	-1 M	0.6		
05/18/82	80.5	7.70	9		0.6	8	-1	0.8		
05/25/82	80.0	7.30			0.1	15	-1	0.8		
06/01/82	86.0	7.55			<0.1	32000	-1			
06/08/82	86.0	7.95	9		<0.1	5738	-1	1.3		
06/15/82	79.0	7.65	6		<0.1	3950	-1			
06/22/82	84.5	7.65	13		<0.1	41700*	-1 M	1.4		
06/29/82	85.0	7.80	13		<0.1	160100	-1	1.4		
07/07/82	84.5	8.05	11		<0.1	98500	-1 M	1.7		
07/13/82	85.0	7.60	11		<0.1	37500	-1 M	1.7		
07/20/82	82.6	7.30	8		<0.1	13000	-1	2.2		
07/27/82	85.5	7.20	8		<0.1	100000	-1	1.0		
08/03/82	83.0	7.65	6		<0.1	35000	-1	0.9		
08/10/82	85.0	7.45	13		<0.1	60000	-1 M	0.8		
08/17/82	82.0	7.10	8		<0.1	30000	-1 H	1.4		
08/25/82	84.0	7.95	2		<0.1	10000	-1 M	1.2		
09/07/82		8.65	3		1.9	3	-1	1.4		
09/14/82	84.5	7.80	2		0.1	15	-1 M	0.9		
09/21/82	83.5	8.60	2		0.6	2	-1	0.5		
09/28/82	79.5	8.45	3		1.1	40	-1	0.5		
10/05/82	81.0	8.30	2		0.4	40	-1	0.9		
10/12/82	83.0	7.70	3		0.2	2	-1	1.0		
10/19/82	74.5	7.90	3		<0.1	210	-1 M	0.8		
10/26/82	76.5	7.90	3		<0.1	4100	-1 M	0.8		
11/02/82	74.0	7.60	3		<0.1	1450		0.8		
11/09/82	68.5	7.65	1		<0.1	170	-1	1.0		
11/16/82	70.0	8.05	2		0.4	2	-1	0.4		
11/22/82	76.0	7.60	4		0.0	28900	-1 M	0.4		
12/07/82	75.0	8.35			0.3	40	-1			
12/14/82	66.5	8.30	2		0.1	38	-1			
12/27/82	68.5									
01/04/83	72.0	7.90	2		2.2	2	-1			
01/11/83	70.5	8.30	4		3.6	6	-1			
01/25/83	65.5	8.75	2		1.3	110	-1			
02/02/83	67.0	8.85	2	19	2.0	90	-1			

(continued)

MELBOURNE DISTRIBUTION SYSTEM (continued)

Table A-4. Banberry Lane and Post Road, northwest corner, 11.3 miles from the South Melbourne Water Treatment Plant. Site No. 4.

DATE	Temp °F	pH	Color cpu pH[1]	Color cpu pH[2]	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
02/16/82	62.0	8.50	1	12	1.4	200	-1			
03/02/83	63.5	8.60	9	16	1.3	400	-1			
03/16/83	64.0	8.20	8	25	0.2	170	-1			
03/30/83	67.0	8.50	3	9	1.7	40	-1			
04/13/83	73.5	8.50	6	26	0.9	50	-1			
04/18/83	71.0	8.80	3		2.3		-1			
05/05/83	78.5	8.55	3		1.9		-1			
05/10/83	78.0	8.70	1		2.0		-1			
05/18/83	79.0	8.50	6		0.5		-1		424	15.1
06/15/83	81.5	8.60	2				-1		431	9.0
06/21/82	83.0	8.55	4	14	2.8	<1	-1	3.2		10.1
07/06/83	84.5	8.05	9	24	2.8	16	-1	4.8		
07/15/83	85.0	8.20	14							
07/18/83	89.0	8.60	22	20	2.1	500	-1	1.9		
07/19/83	86.5	8.55	16				-1		14	

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

*flushed week before

MELBOURNE DISTRIBUTION SYSTEM

Table A-5. 1400 South Apollo Boulevard, West, 15.7 miles from the South Melbourne Water Treatment Plant. Site No. 5.

DATE	Temp °F	pH	Color cpu pH^1	Color cpu pH^2	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
04/20/82	80.0	7.70	6		0.2	1	-1	1.4		
04/27/82	74.5	8.10	4		1.9	1	-1			
05/04/82	76.0	8.40	7		0.1	805	-1	0.7		
05/11/82	77.0	8.30	5		0.4	12	-1	0.7		
05/18/82	80.5	7.90			1.4	7	-1	0.6		
05/25/82	79.5	7.35	7		1.1	5	-1	0.7		
06/01/82	86.0	8.85	8		0.3	49	-1	0.6		
06/08/82	86.0	8.50			1.4	13	-1			
06/15/82	82.0	9.30			3.2	8	-1			
06/22/82	83.0	9.35	9		0.2	136	-1	1.6		
06/29/82	85.0	8.00	10		1.2	21	-1	1.2		
07/07/82	84.5	9.00	16		0.2	58	-1 M	2.5		
07/13/82	85.0	7.70	8		<0.1	1780	-1 M	1.7		
07/20/82	82.0	7.40	6		1.6	5	-1	1.1		
07/27/82	85.5	7.60	8		0.3	40	-1	1.1		
08/03/82	84.0	7.90	6		0.1	2250	-1 M	0.7		
08/10/82	85.0	7.50	4		2.2	5	-1	1.6		
08/17/82	82.0	7.50	9		1.2	10	-1	1.1		
08/25/82	86.0	8.45	8		1.9	10	-1	0.8		
09/07/82		8.95	2		2.3	25	-1	0.4		
09/14/82		8.30			2.4	20	-1			
09/21/82	83.5	9.25	2		3.6	1	-1	0.6		
09/28/82	81.6	8.80	2		1.8	0	-1	0.6		
10/05/82	81.0	8.86	3		1.3	3	-1	1.0		
12/12/82	83.0	8.20	1		2.2	1	-1	0.6		
10/19/82	74.5	8.20	4		<0.1	40	-1 M	0.9		
10/26/82	69.5	8.05	2		0.2	10	-1	0.5		
11/02/82	74.0	8.50	2		1.9	1	-1	0.3		
11/09/82	68.5	9.00	1		3.8	1	-1	0.5		
11/16/82	70.0	8.70	1		3.6	1	-1	0.7		
11/22/82	73.0	8.70	2		2.8	2	-1	0.7		
12/07/82	75.0	8.50			1.8	2	-1			
12/14/82	66.5	8.80	2		3.6	2	-1			
12/27/82	71.0	8.55			3.8	1	-1			
01/04/83	69.5	8.15	2		3.2	20	-1			
01/11/83	67.0	8.75	1		3.8	3	-1			
01/18/83	57.0				2.3		-1			
01/25/83	62.0	8.80	2		1.2	30	-1			

(continued)

MELBOURNE DISTRIBUTION SYSTEM (continued)

Table A-5. 1400 South Apollo Boulevard, West, 15.7 miles from the South Melbourne Water Treatment Plant. Site No. 5.

DATE	Temp °F	pH	Color cpu		Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
			pH[1]	pH[2]						
02/14/83	66.0	8.85	4	8	2.4	5	-1			
03/07/83	70.5	8.45	8	16	1.5	20	-1			22.2
03/28/83	69.5	8.35	3	17	2.4	50	-1			
04/18/83	75.0	8.70	2		2.4		-1			
05/02/83	77.5	8.35	3		1.7		-1			
05/16/83	78.5	8.50	2		1.8		-1 M			
05/18/83	80.5	8.50	2		1.4		-1		445	14.4
06/06/83	82.0	7.95	2	18	2.7	<1	-1			
06/13/83	84.0	8.50	4				-1			
06/16/83					3.2		-1			
06/20/83	83.0	8.00	3	34	1.9	1200	-1		414	
07/06/83	88.0	8.45	4	20	2.9	<1	-1	3.9		
07/12/83	84.5	8.70	8				-1		16	11.6
07/18/83	90.0	8.60	24	18	1.8	1	-1	3.7		

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

MELBOURNE DISTRIBUTION SYSTEM

Table A-6. Palm Bay Meter, Florida and Monroe, 21.3 miles from the South Melbourne Water Treatment Plant. Site No. 6.

DATE	Temp °F	pH	Color cpu pH^1	Color cpu pH^2	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
04/20/82	80.0	8.00	4		0.2	16	-1	0.6		
04/27/82	74.5	8.05	4		0.6	1	-1	0.5		
05/04/82	76.0	7.95	8		0.1	18	-1	0.6		
05/11/82	77.0	8.00	4		0.2	226	-1	0.7		
05/18/82	80.6	7.90			0.2	16	-1	0.6	720	
05/25/82	80.5	7.60	8		0.2	21	-1	0.5		
06/01/82	82.0	8.40	8		0.1	240	-1	0.9		
06/08/82	86.0	8.10			0.1	9	-1			
06/15/82	85.1	8.45			0.3	10	-1		947	
06/22/82	83.5	8.00	8		0.1	81	-1	1.5		
06/29/82	85.0	7.75	0		0.2	850	-1 M	1.2		
07/07/82	84.5	8.25	11		0.1	362750	-1 M	1.0		
07/13/82	85.0	7.80	8		<0.1	98500	-1 M	1.4		
07/20/82	82.0	7.30	4		<0.1	9000	-1 M	2.1		
07/27/82	85.5	7.65	6		<0.1	2000	-1	1.2		
08/03/82	84.0	7.90	6		<0.1	500	-1	0.8		
08/10/82	85.0	7.50	4		<0.1	5500	-1 M	1.3		
08/17/82	82.0	7.45	9		0.1	14500	-1 M	1.4		
08/25/82	86.0	7.80	5		0.2	25000	-1	0.8		
09/07/82	87.0	8.40	2		0.3	0	-1	0.8		
09/14/82		7.80			0.1	160	-1			
09/21/82	83.5	8.80	2		0.3	2	-1	0.7		
09/28/82	81.6	8.15	2		0.2	2	-1	0.9		
10/05/82	81.0	8.50	2		0.1	60	-1	0.8	660	
10/12/82	83.0	7.95	2		0.3	1	-1	0.6		
10/19/82	74.5	8.20	4		0.0	220	-1	0.6		
10/26/82	69.5	7.95	2		<0.1	1560	-1	0.6		
11/02/82	74.0	7.80	2		0.2	70	-1	0.4		
11/09/82	68.5	8.55	2		1.2	2	-1	2.8	570	
11/16/82	70.0	8.30	1		0.9	1	-1	0.6		
11/22/82	73.0	8.45	3		1.2	1	-1	1.9		
12/07/82	75.0	8.45			1.1	50	-1		436	
12/14/82	66.5	8.65	3		<0.1	560	-1		377	
12/27/82	69.5	8.45			2.3	2	-1			
01/04/83	69.5	8.20	2		2.3	1	-1			
01/11/83	67.0	8.50	1		2.7	2	-1			
01/18/83	57.0				1.8		-1			

(continued)

MELBOURNE DISTRIBUTION SYSTEM (continued)

Table A-6. Palm Bay Meter, Florida and Monroe, 21.3 miles from the South Melbourne Water Treatment Plant. Site No. 6.

DATE	Temp °F	pH	Color cpu pH[1]	Color cpu pH[2]	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
01/25/83	62.0	8.75	1		0.6	1	-1			
02/07/83	65.5	8.85	3	11	1.4	1	-1			
02/28/83	70.0	8.45	2	27	1.1	2250	-1			22.6
03/07/83	71.0	8.40	4	10	0.9	50	-1		449	
03/28/83	67.0	8.50	1	8	0.9	0	-1			
04/18/83	73.4	8.80	1		1.9		-1			
04/22/83	71.0						-1			
05/09/83	77.0	8.75	1	7	1.6	1	-1			
05/16/83	80.0	8.50	2	12	0.4	1	-1			
05/17/83	79.0	8.40	2		0.9		-1			
05/24/83	81.0	8.55	2				-1			
06/06/83	84.0	8.40	2	15	1.8	16	-1			
06/13/83	83.0	8.40	2				-1			
06/20/83	83.0	8.60	2	16	2.3	1	-1	1.6		
07/06/83	86.5	8.60	3	8	2.1	<1	-1	0.8		

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

MELBOURNE DISTRIBUTION SYSTEM

Table A-7. Coconut Drive and Sea Avenue, South Side, North Indialantic, 21.7 miles from the South Melbourne Water Treatment Plant. Site No. 7.

DATE	Temp °F	pH	Color cpu pH^1	Color cpu pH^2	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
02/08/83	64.5	8.10	4	21	0.9	5	-1			
02/22/83	67.5	8.55	8	24	2.1	1	-1			
03/21/83	70.5	8.50	7	16	0.8	340	-1			
04/05/83	72.0	8.35	2	11	0.8	220	-1			
04/19/83	71.0	8.40	1	24	1.3	12	-1			
05/03/83	77.0	8.65	2		1.3		-1			
05/24/83	81.0	8.45	1				-1			
05/31/83	82.0	8.20	4	36	1.8	14				
06/14/83	83.0	8.50	1	6	3.2	2	-1	2.3		
06/28/83	85.0	8.45	2	1	1.9	360	-1 M	3.8		
07/07/83	84.5	8.35	2				-1			
07/11/83	85.0	8.70	8	27	2.8	200	-1	5.0		
07/15/83	85.0	8.20	17							
07/25/83	88.0	8.60	23	35	2.4	300	-1 M			

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

MELBOURNE DISTRIBUTION SYSTEM

Table A-8. Ocean Avenue and Pine Street, southwest corner, Melbourne Beach City Hall, 23.3 miles from the South Melbourne Water Treatment Plant. Site No. 8.

DATE	Temp °F	pH	Color cpu		Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
			pH[1]	pH[2]						
01/04/83	69.5	8.10	2		1.6					
01/11/83	67.0	8.25	1		3.2		-1			
01/18/83	57.0				2.1		-1			
01/25/83	62.0	8.75	2		1.2		-1			
02/08/83	67.0	8.60	2	7	0.4	100	-1 M			
02/22/83	65.0	8.30	16	78	0.2	7900	-1			
02/24/83	71.0	8.05			0.2				446	
03/21/83	67.5	8.40	2	17	0.3	1630	-1			
03/02/83	69.8	7.70			0.2				497	
04/05/83	74.5	8.50	6	12	1.1	60	-1			11.5
04/11/83	73.5									11.0
04/19/83	71.0	8.35	1	16	0.3	80	-1			
04/22/83	70.2	7.95			1.6		-1		427	8.5
05/03/83	78.0	8.65	1	13	1.4	24				8.2
05/17/83	79.5	8.45	2	16	0.2	1500	-1		431	11.1
05/24/83	81.0	8.40	2	15	1.3	13				
05/31/83	82.0	8.35	3	13	0.4	16	-1			
06/14/83	84.0	8.20	1	5	2.1	4	-1	2.6		8.4
06/28/83	85.0	8.30	2	19	1.7	84	-1	10		
07/07/83	84.5	8.35	2				-1			
07/11/83	90.0	8.45	6	21	1.8	5000	-1	3.2		11.6
07/13/83	88.0	8.25	11							
07/15/83	85.0	8.00	11				-1			
07/18/83	89.0	8.40	23				-1		25	
07/25/83	91.0	8.60	16	32	2.3	400	-1			9.6

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

MELBOURNE DISTRIBUTION SYSTEM

Table A-9. Ellis Road and Lake Ibis Drive, West Melbourne Meter, 23.3 miles from the South Melbourne Water Treatment Plant. Site No. 9.

DATE	Temp °F	pH	Color cpu pH[1]	pH[2]	Residual mg/l	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/l	TOC mg/L
01/03/83	72.0	8.75	1		5.2		-1			
01/13/83	65.0	8.35	2		5.4		-1			
01/17/83	57.0				4.2		-1			
01/24/83	63.0	8.90	1		4.2		-1			
02/14/83	62.0	8.90	1	12	4.2	2	-1			
02/22/83	64.9	7.90			4.2				259	
02/23/83	66.0	8.80	2	24	2.8	4	-1			
03/02/83	64.4	8.20			3.4				372	
03/09/83	70.7	8.05	6	20	3.6	6	-1			
02/23/83	69.0	8.40	2	8	3.8	4	-1			
04/06/83	73.0	9.00	4		3.8		-1			
04/12/83	74.6	8.70	1	14	3.2	1	-1			9.9
04/15/83	73.5									9.3
04/22/83	72.9	7.75	3		2.6				373	9.2
04/27/83	71.0	8.00		19	3.7	3	-1			
05/09/83	78.0	8.80	4	13	3.2	<1	-1			
05/16/83	78.5	8.85	2	9	4.2	2	-1			
05/18/83	80.5	7.50	9		4.6		-1			12.4
05/23/83	81.0	8.80	2	12	5.2	1	-1		335	
06/06/83	84.0	7.90	2	17	6.2	1	-1		388	10.6
06/21/83	83.0	7.90	8	12	5.4	<1	-1	0.6		
06/27/83	85.0	8.65	3				-1			
07/06/83	84.5	8.30	1	29	4.6	<1	-1	0.7		
07/14/83	85.0	8.00	11				-1			
07/18/83	89.0	8.80	16	17	2.4	2	-1	0.8		
07/19/83	86.5	8.30	14				-1		8	
07/26/83	87.0	8.55	9				-1			8.9
07/31/83					3.2		-1			

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

MELBOURNE DISTRIBUTION SYSTEM

Table A-10. Carriage Road, 3/4 mile from Desoto and St. Patrick Drive, Indian Harbour Beach, 23.9 miles from the South Melbourne Water Treatment Plant. Site No. 10.

DATE	Temp °F	pH	Color cpu pH[1]	pH[2]	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
02/01/83	68.0	7.6	3	16.4	0.0	1330	-1 M			
02/15/83	66.5	7.6	3	12.0	<0.1	650	-1 M			
03/08/83	71.0	7.8	4	10.0	0.0	2020	-1 M			
03/29/83	67.0	7.6	2	8.0	0.0	3330	-1 M			
04/12/83	73.5	7.4	1	<0.1			-1 M			
Start at DeSoto next sample										
05/31/83	82.0	8.2	7	28.8	0.2	60				
06/09/83	82.0	7.9	3				-1			
06/14/83	83.0	8.1	1	7	0.2	35	-1	1.6		
06/28/83	85.0	8.2	2	8	0.8	<1	-1	3.6		
07/11/83	86.0	8.6	8	27.2	2.6	48	-1	1.6	30	
07/25/83	88.0	8.6	18	32	2.3	88	-1			
07/28/83	86.0	8.6	16				-1			

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

MELBOURNE DISTRIBUTION SYSTEM

Table A-11. 436 North Waterway Drive, South Patrick Shores, 27.0 miles from the South Melbourne Water Treatment Plant. Site No. 11.

DATE	Temp °F	pH	Color cpu		Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
			pH^1	pH^2						
04/20/82	78.5	8.10	4		0.2	343	-1 M	1.1		
04/27/82	77.5		6		0.2	1010	+ H	6.4		
05/04/82	76.0	7.85	10		0.2	124	-1 H	2.0		
05/11/82	78.0	7.95	3		0.1	370	-1 H	0.7		
05/18/82	80.5	7.60			0.1	510	-1 H			
05/25/82	80.0	7.30	9		0.1	450	-1 M	2.8		
06/01/82	82.0	8.35	11		<0.1	4230	-1 M	3.2		
06/08/82	86.0	7.80			<0.1	1340	-1 M			
06/15/82	88.0	8.10			<0.1	880	-1 H		1284	
06/22/82	84.5	7.45	11		<0.1	260	-1 M	4.8		
06/29/82	85.0	7.80	12		<0.1	7100	-1 H	3.2		
07/07/82	84.5	7.80	16		<0.1	8050	-1 M	2.4		
07/13/82	85.0	7.75	9		<0.1	5950	-1 M	1.6		
07/20/82	82.0	7.45	9		<0.1	550	-1 M	2.0		
07/27/82	85.5	7.55	8		<0.1	4400	-1 M	1.5		
08/03/82	87.0	7.50	8		<0.1	2650	-1 M	1.6		
08/10/82	85.0	7.30	8		<0.1	6000		3.1		
08/17/82	82.0	7.50	8		<0.1	2500	-1 M	1.8		
08/25/82	87.0	7.80	6		<0.1	1100	-1 M	1.8		
09/07/82	88.0	8.00	4		0.1	260	-1 M	0.6	814	
09/14/82		7.84	1		<0.1	75	-1 M	0.7		
09/21/82	83.5	8.20	2		0.0	90	-1 M	0.8		
09/28/82	81.6	8.00	1		0.0	180	-1 M	0.7		
10/05/82	81.0	8.50	4		<0.1	180	-1 M	1.0		
10/12/82	83.0	7.80	1		0.0	40	-1 M	0.6	887	
10/19/82	74.5	7.70	3		0.0	90	-1 M	0.8		
10/26/82	78.5	7.75	3		0.0	920	-1 M	0.9		
11/02/82	74.0	7.65	3		0.0	14950	-1 M	1.3		
11/09/82	68.5	8.05	1		<0.1	300	-1 M	0.4	705	
11/15/82	70.0	8.10	2		0.0	6400	-1 M	0.9		
11/22/82	77.5	8.25	2		0.0	200	-1 M	0.2		
12/07/82	75.0	8.20			0.0	460	-1 M		608	
12/14/82	74.5	8.10	2		0.0	1830	-1 M		553	
12/27/82	73.0	8.15			<0.1	120	-1			
01/04/83	73.5				0.6	260	-1			
01/11/83	67.0	7.95	2		2.8	1	-1			
01/18/83	57.0	8.45	2		1.9		-1			
01/25/83	67.5	8.35	2		1.2	6	-1			

(continued)

MELBOURNE DISTRIBUTION SYSTEM (continued)

Table A-11. 436 North Waterway Drive, South Patrick Shores, 27.0 miles from the South Melbourne Water Treatment Plant. Site No. 11.

DATE	Temp °F	pH	Color cpu pH[1]	Color cpu pH[2]	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
02/01/82	68.0	8.75	2		2.6	0	-1			
02/15/82	62.0	8.90	1		1.3	3	-1			
03/08/83	71.0	8.75	1		0.3	10	-1			
03/29/83	67.0	8.40	4		0.9	20	-1			
04/12/83	73.5	8.40	2		0.3		-1			
04/22/83	23.8									
04/26/82	75.0	8.35	2		0.0		-1			
05/17/83	79.5	8.20	2		<0.1		-1			
05/31/83	82.0	8.30	4	12	1.1	2				
06/09/83	82.0	8.05	2							9.5
06/14/83	83.0	8.30	1	5	1.4	1	-1	0.8		8.7
06/28/83	85.0	8.00	3	1	0.2	240	-1	6.5		
07/11/83	86.0	8.70	11	17	2.8	1	-1	2.1		
07/15/83	85.0	8.45	17							
07/25/83	88.0	8.60	17	27	1.9	39	-1			9.2
07/28/83	86.0	8.70	9				-1			

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

Table A-12. Riverwalk Drive and Seacrest Drive, southeast corner, South Melbourne Beach, 29.3 miles from the South Melbourne Water Treatment Plant. Site No. 12.

DATE	Temp °F	pH	Color cpu pH[1]	Color cpu pH[2]	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
04/20/82	80.0	7.30	6		0.2	30950	-1	0.8		
04/27/82	74.5	7.70	4		0.2	1250	-1 M	0.6		
05/04/82	76.0	7.70	6		0.1	5800	-1 M	0.7		
05/11/82	77.0	7.95	4		0.1	1785	-1	1.0		
05/18/82	80.5	7.55			0.1	1130	-1		870	
05/25/82	80.0	7.30	9		0.1	7600	-1 M	1.0		
06/01/82	82.0	7.55	9		<0.1	2240	-1	1.0		
06/08/82	86.0	7.80			<0.1	280	-1 M			
06/15/82	85.1	7.85			<0.1	3800	-1 M		1124	
06/22/82	84.5	7.95	6		<0.1	390	-1 M	1.1		
06/29/82	85.0	7.70	8		<0.1	27950	-1 M	1.0		
07/07/82	86.0	8.10	16		<0.1	43500	-1 M	1.6		
07/13/82	85.0	7.45	8		<0.1	119000	-1 M	1.1		
07/20/82	82.0	7.15	8		<0.1	5500	-1 M	2.0		
07/27/82	85.5	7.45	8		<0.1	21000	-1	1.0		
08/02/82	84.0	7.40	8		<0.1	10000	-1	1.0		
08/10/82	85.0	7.50			<0.1	4500	-1 M	1.0		
08/17/82	82.0	7.30	6		<0.1	20000	-1	1.2		
08/25/82	86.0	7.70	4		<0.1	31750	-1 M	0.9		
09/07/82		7.75	3		0.0	25400	-1	0.9		
09/14/82		7.90	2		<0.1	13400	-1 M	0.6		
09/21/82	83.5	7.90	3		0.0	240	-1 M	0.8		
09/28/82	81.6	8.20	2		0.0	640	-1	0.6		
10/05/82	81.0	7.95	3		<0.1	1000	-1	1.0		
10/12/82	83.0	7.65	±		<0.1	1760	-1	0.6		
10/19/82	74.5	7.65	4		<0.1	300	-1 M	0.6		
10/26/82	69.5	7.60	3		0.0	11450	-1 H	0.4		
11/02/82	74.0	7.55	3		0.0	8000	-1 M	0.5		
11/09/82	68.5	7.70	3		<0.1	9050	-1 M	0.8		
11/16/82	70.0	7.90	1		0.0	13000	-1 M	0.7		
11/22/82	73.0	8.00	14		<0.1	107500	-1	9.4		
12/07/82	75.0	8.25			0.1	2740	-1 M			
12/14/82	66.5	7.85	2		<0.1	34500	-1 M		585	
12/27/82	72.5	7.90			0.0	128500	-1			
01/04/83	69.5	7.55	2		<0.1	248000	-1 M			
01/11/83	67.0	7.90	1		0.0	10200	-1			
01/18/83	57.0				<0.1		-1 M			

(continued)

MELBOURNE DISTRIBUTION SYSTEM (continued)

Table A-12. Riverwalk Drive and Seacrest Drive, southeast corner, South Melbourne Beach, 29.3 miles from the South Melbourne Water Treatment Plant. Site No. 12.

DATE	Temp °F	pH	Color cpu pH^1	Color cpu pH^2	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
01/25/83	62.0	8.60	1		<0.1	163000	-1 M			
02/08/83	61.5	8.50	1		<0.1	630	-1 M			
02/22/83	65.0	8.30	17		<0.1	69000	-1 M			
03/21/83	67.5	8.30	1		<0.1	15750	-1		448	
04/05/83	72.0	8.25	3		<0.1	1300	-1			
04/19/83	76.0	8.05	1		<0.1	22000	-1 H			8.6
05/03/83	77.0	7.95	2		<0.1		-1			
05/18/83	80.5	8.10	2		<0.1		-1 M		512	14.5
05/24/83	81.0	8.00	2				-1			
05/31/83	86.0	8.35	4	35	<0.1	24400				
06/14/83	84.5	7.80	1	6	<0.1	65000	-1 M	0.8		8.6
06/28/83	85.0	7.80	2	1	<0.1	20000	-1 M	1.1		
06/29/83	84.5	7.90	2				-1 M			
07/07/83	84.5	8.10	1				-1 M			
07/11/83	85.0	8.25	4	13	0.55	23000	-1 M	0.8		
07/18/83	84.5	8.10	16				-1			
07/25/83	88.0	8.45	8	20	1.3	24	-1			8.7

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

MELBOURNE DISTRIBUTION SYSTEM

Table A-13. North A1A Highway (Between N.E. 3rd Street and Ocean Boulevard) 28.9 miles from the South Melbourne Water Treatment Plant. Site No. 13.

DATE	Temp °F	pH	Color cpu pH[1]	Color cpu pH[2]	Residual mg/L	SPC #/mL	MF #/mL	Turb NTU	THMFP µg/L	TOC mg/L
02/01/83	68.0	8.50	1	6.8	0.3	70	-1			
02/15/83	66.5	8.45	2	4.4	<0.1	80	-1			
03/08/83	71.0	8.25			0.0	900	-1			
03/29/83	67.0	8.20			<0.1	800	-1			
02/22/83	67.0								558	
03/02/83									549	
05/17/83	79.0	8.20	2	4	0.1	860			465	
05/31/83	83.0	8.00	4	16.4	<0.1	600				
06/09/83	82.0	7.75	1				-1 M			
06/14/83	82.5	8.00	2	6	<0.1	2770	-1	0.6		8.0
06/28/83	85.0	7.90	2	4	<0.1	32000	-1 H	1.3		
06/29/83	84.5	8.05	2				-1 H		678	9.1
07/11/83	87.0	8.20	6	24.4	0.9	5000	-1	8.2		10.8
07/25/83	89.0	8.45	8	24	1.4	57	-1		33	
07/28/83	86.0	8.65	16				-1			

[1] pH not adjusted for color measurement

[2] pH adjusted for color measurement

APPENDIX A.2

SAS Data Sheets

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                                              WATER QUALITY STUDY
21:03 TUESDAY, AUGUST 17, 1982
                                         -----  REDUCED ITHM DATA SET  -----
                                              FULL NATURAL LOG MODEL
                                                 EQUATION RTHM3
                                      LNTHM = LNCLA LNIEMP LNTOC LNPH LNTIME


                              GENERAL LINEAR MODELS PROCEDURE

DEPENDENT VARIABLE:  LNTHM
SOURCE     OF       SUM OF SQUARES      MEAN SQUARE                 F VALUE           PR > F   R-SQUARE    C.V.
MODEL               5  687.06145379      137.41229076                3332.96           0.0001   0.970588    99.0974

ERROR             505   20.82026950        0.04122826       STD DEV                            LNTHM MEAN

CORRECTED TOTAL 510  707.88172329                           0.20304742                         -0.20489680

SOURCE              OF   TYPE I SS       F VALUE     PR > F   OF        TYPE IV SS              F VALUE     PR > F

LNCLA                1  118.24772543     2888.12     0.0001   1        13.16605765               319.35     0.0001
LNTEMP               1    0.43049019       10.44     0.0013   1         4.60736420               111.75     0.0001
LNTOC                1  286.37974481     6946.20     0.0001   1       380.10979460              9219.64     0.0001
LNPH                 1   42.53493279     1031.691    0.0001   1        47.02788587              1140.67     0.0001
LNTIME               1  239.46846056     5808.36     0.0001   1       239.46846056              5808.36     0.0006

                                   I FOR HO:                     STD ERROR OF
PARAMETER          ESTIMATE     PARAMETER=0       PR > ITI       ESTIMATE

INTERCEPT        0.69774485         13.72          0.0001      0.05087326
LNCLA            0.21440157         17.87          0.0001      0.01199769
LNTEMP           0.17056110         10.57          0.0001      0.01613435
LNTOC            1.24624060         96.02          0.0001      0.01297911
LNPH             0.09523156         33.77          0.0001      0.00281969
LNTIME           0.25964311         76.21          0.0001      0.00340683
```